THE PROCEEDINGS OF
THE PHYSICAL SOCIETY

VOL. 41, PART 3 *April* 15, 1929 NO. 228

THE PHOTOGRAPHIC MEASUREMENT OF THE RELATIVE INTENSITIES OF THE $L\alpha_1$, α_2, α_3 LINES OF SILVER

BY H. C. WEBSTER, M.Sc.
Dixon Research Scholar, Natural Philosophy Laboratory, University of Melbourne

Received December 10, 1928. *Read and discussed February* 8, 1929

ABSTRACT. A knowledge of X-ray line intensity is needed in the theory of atomic structure and in chemical analysis by means of X-rays. The relative advantages of the ionization, Geiger counter, and photographic methods of measurement are discussed. The advantages of the photographic method are that (1) a permanent record is obtained, and (2) the photographic effect is cumulative, a condition which is especially valuable for lines of weak intensity. Its disadvantages are the difficulty of deducing the intensity from the blackening of the emulsion, and the care needed in development and photometry. The ionization method requires a steadier source of radiation, and difficulties arise owing to "end" effects, Compton scattering, and internal absorption of characteristic X-rays. The Geiger counter method counts the quanta, but the unjustifiable assumption is made that the number of electrons ejected from a metal foil by X-rays, on the side of incidence, depends only on the number of incident quanta. In the photographic method used by the author the densities, D, of the photographic images of the lines, produced by a vacuum spectrograph, are measured by means of a Moll micro-photometer. The density is a function of the exposure, the frequency, the photographic emulsion, and the development. This function is discussed. Previous work has shown that the Bunsen-Roscoe reciprocity law applies in the case of X-rays, and it is shown that for constant development, and for the range of frequencies measured, D is a function of Nt, where N is the number of quanta absorbed per second in the emulsion and t the exposure time. This function is found by varying t. Corrections are made for the overlapping of the lines. The results obtained are: $L\alpha_1 : L\alpha_2$, 100 : 12·0; $L\alpha_1 : L\alpha_3$, from 100 : 4·6 to 100 : 7·3, according to the tube voltage. A value of $L\alpha_1 : L\beta_1$, of less accuracy, is found as 100 : 40.

§ 1. INTRODUCTION

A KNOWLEDGE of the relative intensities of lines in X-ray spectra is necessary for the verification of the many theories of the atom which have recently been put forward. Further, in an investigation which has recently been made in this laboratory of chemical analysis by X-rays it has become evident that if that method, which has been found to be highly sensitive, is to be made quantitative, a knowledge of X-ray line intensities and particularly of the "photographic" intensities is essential.

Definition

In this paper the intensity of an X-ray line of frequency ν is defined as the number of quanta of *characteristic* radiation of this frequency (general radiation being thus excluded) which proceed per second from the anticathode in the X-ray tube.

Methods of measurement

Three methods have been employed in measuring the intensity of X-ray lines. All these depend upon a secondary effect of the X-rays, namely the ionization produced by the photo-electrons ejected by the X-rays in some material.

The ionization method, developed chiefly by Duane and his collaborators*, is the method most frequently employed. Here the photo-electrons are ejected from a gas in which the X-radiation is absorbed and the current thus permitted to pass is registered.

In Jonsson's method† the photo-electrons ejected from a metal foil are counted by Geiger's device.

In the photographic method the photo-electrons ejected in the emulsion render the silver halide grains developable. This method, as applied to X-ray intensities, owes its development chiefly to Friedrich and Koch‡, Glocker and Traub§, Allen and Laby||, and Bouwers¶, and has been applied to the measurement of relative intensities of lines by Siegbahn and Zacek**.

The advantages of the photographic method are that (1) a permanent record is obtained; (2) the photographic effect is cumulative. This condition is especially valuable in the case of lines of very small intensity, and it averages out short-period variations in the intensity of the source.

The disadvantages of the method are (1) the difficulty of deducing the intensity of the X-rays from the blackening they produce in the photographic emulsion; (2) the care necessary in photometry; and (3) the care necessary in development.

The disadvantages of the ionization method are as follows: (1) Very steady sources of X-rays are needed, except when a balance method is used. (The balance method introduces complexity.) (2) Some of the ionization produced by photo-electrons ejected from the gas in the vicinity of the ends of the electrodes in the ionization chamber is not recorded. Since the manner of distribution in space of the directions of ejection is not satisfactorily known, the necessary corrections cannot be accurately estimated. (3) The relation between the number of photo-electrons and the number of quanta entering the chamber is complicated by

---

* Duane and Stenstrom, *Nat. Acad. Sci. Proc.* **6**, 477 (1920). Duane and Patterson, *Ibid.* **6**, 526 (1920); **8**, 89 (1922).

† Jonsson, *Zeits. für Phys.* **36**, 426 (1926); **41**, 221, 801 (1927); **46**, 383 (1928).

‡ Friedrich and Koch, *Ann. der Phys.* **45**, 399 (1914).

§ Glocker and Traub, *Phys. Zeits.* **22**, 345 (1921).

|| Allen and Laby, *Proc. Roy. Soc. Vic.* **31**, 421 (1919).

¶ Bouwers, *Over het meten der Intensiteit van Rontgenstralen: Einthoven* (1924).

** Siegbahn and Zacek, *Ann. der Phys.* **71**, 187 (1923).

Compton scattering and internal absorption of characteristic X-radiations, and thus difficulties arise in determining the relation between the ionization and the number of quanta.

Jonsson claims that the ratio between the (corrected) observations with the Geiger counter and the number of entrant X-ray quanta is a constant independent of the wave-length. This assumption is not justifiable, since the fraction of the electrons ejected below the surface of the foil which actually produce discharges will depend on the mean depth of ejection and hence on the wave-length of the X-rays. Further disadvantages are: (1) the difficulty of obtaining counter needles which discharge for every photo-electron, and give no spurious effects; also the gradual deterioration of such needles; (2) the fact that since it is inconvenient to prolong considerably the time occupied by each observation, the method is less suitable than the photographic for very weak lines.

§ 2. THE PHOTOGRAPHIC METHOD

The density of an element of area of the film depends on the following factors: (1) the function

$$F'(N_1, dt_1, N_2, dt_2, \ldots\ldots),$$

where N_1 represents the number of quanta of radiation absorbed in the emulsion during the element of time dt_1, at the commencement of the exposure, and so on, dt_2, dt_3, ... being successive elements of time; (2) the frequency ν of the radiation; (3) the emulsion; (4) the developer; (5) the time of development; (6) the temperature of the developer. Other factors have a minor influence.

Assuming that the last four of the above factors are constant and such as are found satisfactory in X-ray photography, it follows that

$$D = F''(N_1, dt_1, N_2, dt_2, \ldots\ldots, \nu).$$

The important case is when N either is constant during the exposure, or varies in a regular, rapid cycle which has some definite "wave-form," as is the case when all the radiations coming into consideration have the same excitation potential and are excited by means of an alternating potential.

It then follows that

$$D = F(N, t, \nu),$$

where N denotes the mean value.

In the usual methods of optical spectro-photometry* the time factor is eliminated, since the exposure times for all lines are the same, a scale of densities being formed along the length of each line by means of a calibrated absorption wedge, and the relative intensities obtained by matching portions of equal density. No determination of X-ray line intensities by this method has, however, yet been reported, the difficulty being the obtaining of suitable wedges.

---

* Dobson, Griffiths, and Harrison, *Photographic Photometry*, pp. 28–55; Dorgelo, *Phys. Zeits.* **26**, 756 (1925).

For light of given frequency, Kron* and others† have found certain complex empirical expressions for the function F, which reduce, for small ranges of intensity, to the Schwarzschild‡ relation:

$$D = F(Nt^p),$$

where p is of the order of 0·9, the source being steady.

As regards sources with rapid and regular intermissions, the experiments of Weber§ and Howe|| indicate that, provided the total exposure time is constant,

$$D = f(NT),$$

where T is the portion of the total time during which the radiation was incident on the film. If, as is fairly justifiable, it be assumed that this property applies in the case of X-rays also, it follows that for fluctuating sources the expression

$$D = F(N, t, \nu)$$

applies even if the "wave-forms" for the radiations considered are not identical.

Glocker and Traub¶, and also Bouwers**, have verified the validity of the Schwarzschild law in the X-ray region, using an intermittent source of radiation such as that provided by a transformer with mechanical rectifier. The mean value obtained for p was 0·98, but within the limits of experimental error the assumption of the Bunsen-Roscoe reciprocity law

$$D = F(Nt) \qquad (\nu \text{ being constant})$$

was justified. The maximum ratio of the intensities used was 1 : 9.

The X-ray tube used in the experiments to be described was connected directly to the secondary of a transformer fed with a.c. of 50 cycles per second, the current through the tube being thus a pulsating one similar to that used by Bouwers. It is assumed that the amplitude and form of the pulses used by the author were constant.

Experiments, which will be described later, showed that for silver L radiation excited in this way the reciprocity law was valid within the limits of experimental error.

In radiation reflected from a rocking crystal, as used in the work to be described, the intensity incident on any element of area of the film varies with the position of the crystal. This causes no error, however, since the reciprocity law is valid. It is worthy of note that the range of validity is likely to be larger than usual, on account of the rapid cyclic character of the variation in intensity.

Berthold†† has examined the relation between the photographic density and the

---

[*] Kron, *Ann. der Phys.* **41**, 751 (1913).

[†] Parkhurst, *Astrophys. Journ.* **30**, 33 (1909); Ives, *Ibid.* **31**, 157 (1910); Jones and Huse, *Journ. Opt. Soc. Amer.* **7**, 1079 (1923); **11**, 319 (1925).

[‡] Schwarzschild, *Astrophys. Journ.* **11**, 89 (1900).

[§] Weber, *Ann. der Phys.* **45**, 801 (1914).

[||] Howe, *Phys. Rev.* **8**, 674 (1916).

[¶] Glocker and Traub, *Phys. Zeits.* **22**, 345 (1921).

[**] Bouwers, *Over het meten der Intensiteit van Rontgenstralen: Einthoven* (1924).

[††] Berthold, *Ann. der Phys.* **76**, 409 (1925).

ionization current for several wave-lengths between 0·15 and 1·9 Å.U. He determined, in effect, the relative numbers of quanta of various frequencies the absorption of which in the emulsion produced a given density, thus avoiding reference to blackening laws. His final results are contained in the expression:

$$n \propto \lambda/(15{\cdot}83 - 1/\lambda), \qquad \text{where } \lambda \text{ is in Å.U.}$$

The measurements of Barkla and Martyn* of the same relation gave results in fair accord with the above expression.

Bouwers† has compared the photographic density produced spectroscopically by radiations of a few different frequencies with the energy of the incident (filtered) radiation, measured bolometrically. His results, expressed in terms of the number n, as above, are as follows, the values computed from Berthold's expression being inserted for comparison:

Table 1.

Wave-length (Å.U.)	0·19	0·22	0·47	0·56	0·71
n (Bouwers)	1	1·05	2·22	2·30	2·22
n (Berthold)	1	1·05	1·91	2·22	2·77

The results of Allen and Laby‡ are not directly comparable, since they related to heterogeneous radiation. These authors found that the density produced by the general radiation from a Coolidge tube excited by potentials of 31·5, 73, and 83 kilovolts was proportional to the quantity of electricity which passed through the tube and to the square of the applied potential.

The above results show that, within the limited ranges of frequency used in the experiments to be described, it is justifiable to assume that the density depends on the number of quanta absorbed, but not on the frequency.

The influence of the emulsion and also of the development are of the same nature as for light, and the conditions for optimum development are also the same.

§ 3. EXPERIMENT

A spectrograph with a common vacuum for the spectrograph and X-ray tube, as used by Shearer§ in this laboratory, was employed, the crystal and camera being operated through conical joints as in Siegbahn's|| design. The main features of this apparatus are illustrated in Figs. 1 and 2.

The only features needing comment are (1) a lapped joint at D, Fig. 2, which allowed the ready removal of the anticathode for cleaning, and accurate re-assembly; (2) a rubber ring H which permitted the ready adjustment of the orientation of the X-ray tube relative to the spectrograph. The principal slit K was 0·1 mm. wide and the slit M about 1 mm.

Spectrograph and X-ray tube were evacuated by separate Gaede diffusion pumps, backed by the same Hyvac pump. A mercury trap, with freezing mixture,

---

* Barkla and Martyn, *Phil. Mag.* **25**, 296 (1913).

† Bouwers, *Over het meten der Intensiteit van Rontgenstralen: Einthoven* (1924).

‡ Allen and Laby, *Proc. Roy. Soc. Vic.* **31**, 421 (1919).

§ Shearer, *Phil. Mag.* **4**, 745 (1927).

|| Siegbahn, *The Spectroscopy of X-Rays*, pp. 63–65.

was inserted between the X-ray tube and its pump. Calculations showed that, on account of the high resistance of the slit *K* to the flow of gas at low pressures, a much lower pressure should be obtainable in the X-ray tube than in the spectrograph, where castor oil is present. The steadiness of the running of the X-ray tube indicated a satisfactory vacuum therein and showed the advantage of having two pumps connected as described.

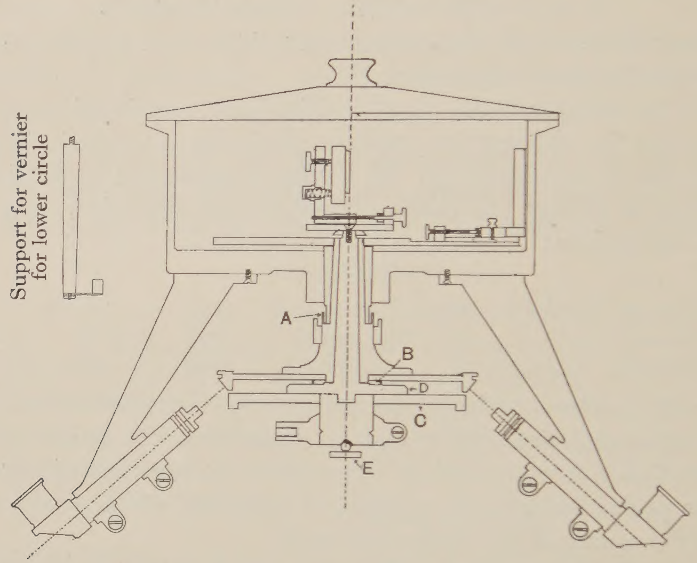


Fig. 1. Sectional side elevation of spectrograph.

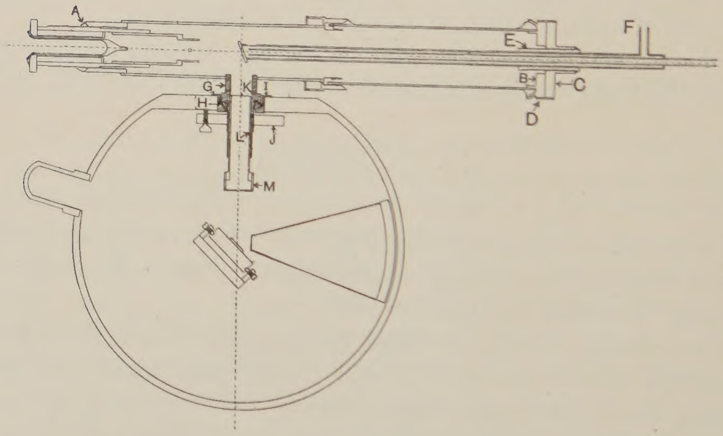


Fig. 2. Sectional plan of spectrograph.

The tube was fed directly from a 20 kv. transformer. Tungsten was first used for the filament, but later a Wehnelt filament proved very satisfactory. A small auxiliary voltage was sometimes applied to the hood in the latter case. Suitable rheostats permitted fine control of the tube voltage and current, the fluctuations of these being of the order of 1 per cent. The crystal was rocked by the usual cam mechanism, the sweep being amply sufficient to cover the reflection angles of all three lines $L\alpha_1$, α_2, α_3.

With the tungsten filament, but not with the Wehnelt, a screen of carbon paper covered the end of the camera. Calculations showed that the correction for the different absorptions in this of the $L\alpha_1$, α_2, α_3 was negligible. A series of exposures was taken on each film (Kodak Radia-tized Dental X-Ray) for times adjusted to give suitable densities for the various lines and to permit the convenient construction of calibration curves as described later. The film was developed for five minutes at 18·7° C. in the solution recommended by the Eastman Kodak Co., these being the optimum conditions specified by them.

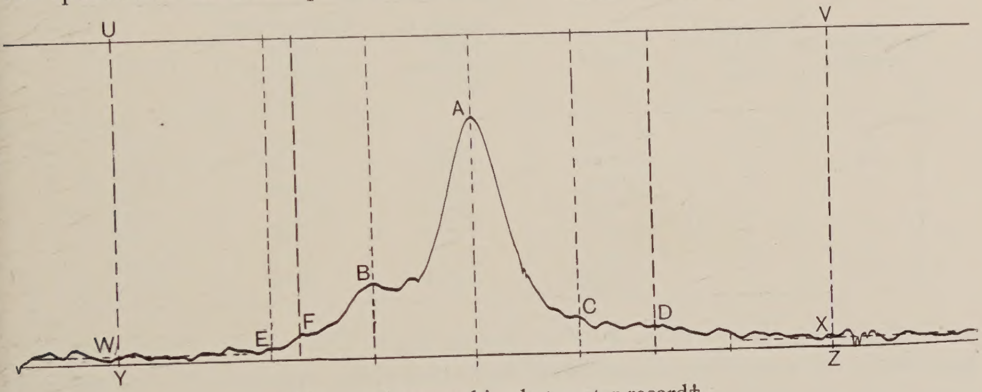


Fig. 3. Photographic photometer record[†].

The film was photometered in a micro-photometer of the Moll type. Care was taken that the portions of the various lines photometered had been exposed at the same place in the spectrograph. To eliminate galvanometer lag the speed of translation of the film was made small, namely about 2·5 mm. per hour.

Each photographic photometer record (see Fig. 3) refers to all portions of the film subject to reflected X-radiation during the corresponding exposure. The zero line *UV* was determined by running the apparatus with the photometer lamp off for a few minutes immediately before and after the run, a procedure which gave two small sections near *U* and *V* respectively. For the dupli-tized film used the densities should strictly be obtained from the light incident on and emergent from the "front" emulsion, but since the "back" emulsion is very little affected by the X-rays, which are strongly absorbed in the front emulsion and the celluloid, and since the latter has constant photometric density, the foregoing theory may be applied to the densities of the film as a whole in determining the intensities. The line *YZ* represents the light intensity incident on the film during the photometer run. To obtain *YZ* observations were made, with a scale replacing the photographic paper, of the densities of the uniform portions of the film on either side

---

[*] Eastman Kodak Co. pamphlet *X-Rays*, pp. 36–38.

[†] Note: The line *YZ* should actually occupy a position 6 cm. (in the original) farther away from *UV*, but was moved up so as to bring it on to the photographic paper.

of the spectral image considered. The distances *UY* and *VZ*, representing the incident light intensities corresponding to the transmitted intensities *UW* and *VX*, respectively, could be determined. Owing to a slight regular variation in the emission of the photometer lamp, *UY* and *VZ* differed slightly. It could, however, be assumed, with fair accuracy, that points on *YZ* gave the incident intensities proper to the corresponding points on the photographic record.

From the three lines *UV*, *WX*, *YZ* the densities of the various elements of area of the film could be obtained. Table 2 contains the measurements at the maximum of $L\alpha_1$ (point *A*) on the photometric curves for film C 207.

Table 2.

Image number	Exposure (t) in min.	Log t	Incident light intensity (cm.)	Transmitted light intensity (cm.)	Density
4	16	1·204	14·87	0·05	2·473
5	10	1·000	13·90	0·22	1·801
6	7	0·845	14·04	0·32	1·632
7	5	0·699	14·10	0·80	1·246
8	3	0·477	14·46	2·48	0·766
9	2	0·301	14·59	4·07	0·554
10	1	0·000	14·52	6·00	0·384

A graph was drawn (Fig. 4) of D against $\log t$. The relative "photographic" intensity at the maximum of $L\alpha_2$ (point *B*) to that at the maximum of $L\alpha_1$ (point *A*) could then be obtained by determining the time t' which corresponded on the graph to the density at *B*, for by the reciprocity law

$$Nt = Nt',$$

where t is the actual exposure time.

To obtain the true relative intensities, the following considerations had to be taken into account*. (1) According to definition the general radiation must be excluded in determining the relative intensities. Measurements showed, however, that the density due to general radiation was so small that the corrections to be applied to the relative intensity measurements were negligible. (2) Owing to the differences of absorption in the film for the different lines, the relative numbers of quanta absorbed in the film are not equal to the relative numbers of incident quanta. Calculations showed that the error was of the order of 1 per cent., and since, further, this correction is in the opposite direction to that for variation in sensitivity with wave-length (by Berthold's expression given previously), it was neglected. (3) The lines overlap. For estimation of the correction an α_2 calibration curve was drawn analogous to the α_1 curve, and intensities at various other points were determined from the curve, relative to that at the peak of $L\alpha_2$. The assumption was now made that all the lines were symmetrical and of the same shape.

---

* *Note:* The variation with wave-length of the reflective power of the crystal gives rise to no appreciable error with the limited wave-length range and good calcite crystal used. Cf. Davis and Stempel, *Phys. Rev.* 17, 608 (1921); Wagner and Kulenkampff, *Ann. der Phys.* **68**, 369 (1922).

Then the intensity at a point C at the same distance as the α_2 peak from the α_1 peak, but on the opposite side, gave, subject to correction on account of a contribution due to α_3, the portion of the intensity at the peak of $L\alpha_2$ due to $L\alpha_1$. The intensity at the peak of $L\alpha_3$ (point D) needed no appreciable correction for the overlapping of $L\alpha_1$, and the ratio between this intensity and the portion of the intensity at C due to α_3 could be assumed to be equal to the ratio between the intensity at the peak B of $L\alpha_2$ and that at a point F at a distance from this peak equal to the distance between D and C. The intensity at a point E at the same distance as the α_1 peak from the α_2, but on the opposite side, gave the portion of the intensity at the peak of $L\alpha_1$ due to $L\alpha_2$.

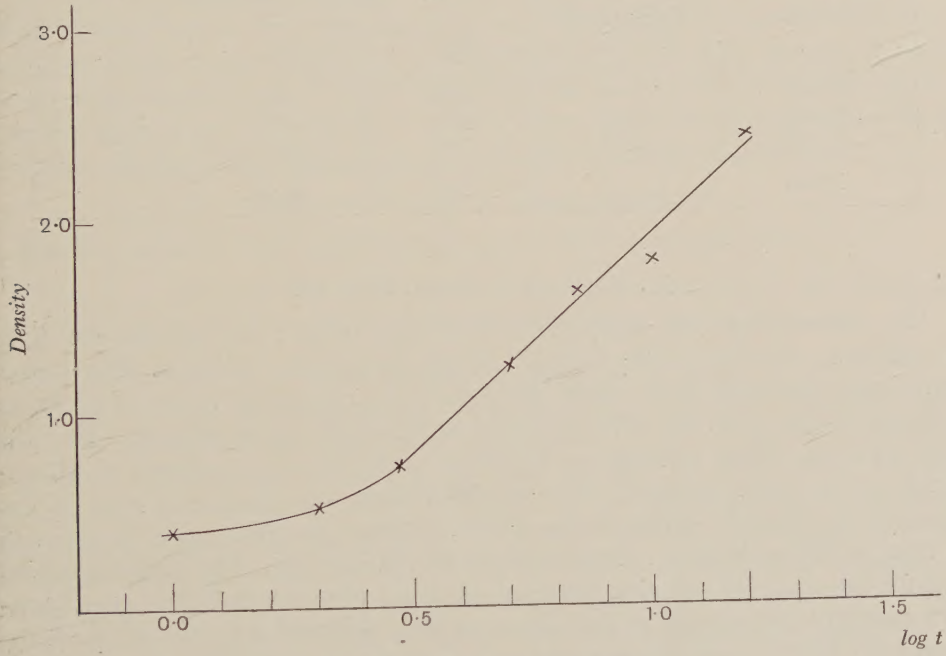


Fig. 4. Density/exposure curve.

The intensities for film G 104 are collected in Table 3:

Table 3.

Intensity at	Spectral image 1	Spectral image 2	Spectral image 3
A	100	100	100
B	17·3	19·0	21·1
C	7·6	8·5	11·2
D	6·9	7·1	7·8
E	2·7	2·9	3·4
F	3·5	3·8	4·5
La_3 at C	1·2	1·5	1·8
La_1 at B	6·4	7·0	9·4
La_2 (corrected)	10·9	12·0	11·7
La_1 (corrected)	97·3	97·1	96·6

§ 4. RESULTS

The intensity ratio for $L\alpha_1 : L\alpha_2$ given in Table 4 is in fair accord with the ratio, 100 : 11·1, predicted by Sommerfeld's theory of X-ray line intensities, and thus affords support to the Stoner-Smith theory of electron distribution. The increase of the relative intensity of $L\alpha_3$ with increasing tube voltage is to be expected if $L\alpha_3$ has a higher critical voltage than $L\alpha_{1,2}$, in accordance with the usually accepted theory of X-ray spark lines*.

Table 4.

Film no	Tube voltage (R.M.S.)	Relative intensities		
		$L\alpha_1$	$L\alpha_2$	$L\alpha_3$
C 207	—	100	12·0	5·8
G 104	20·0	100	11·8	7·3
G 106	16·2	100	12·2	4·6
Mean		100	12·0	

§ 5. THE RECIPROCITY LAW

The tube voltage was adjusted to about 3000 volts r.m.s., so that the silver *L* radiations constituted the majority of the short-wave radiation. The longer wave-length radiations were largely filtered out by an aluminium sheet of thickness sufficient to cut down the silver $L\alpha$ to about one-tenth of its intensity. The slits were removed. Three portions cut from the same film were mounted on attachments to the camera support, and a special shutter was attached in place of the crystal table. Thus by means of the conical bearings the films could be exposed, in turn, at different known distances from the anticathode. Calculations showed that the intensities of radiation falling on the films were to a sufficient approximation inversely proportional to the squares of their distances from the centre of the focal spot. The times of exposure were made inversely proportional to the computed intensities and the measurement of the resultant densities provided a test for the reciprocity law. Results obtained are given in Table 5.

Table 5.

Intensity	Densities	
	Films G 112–4	Films G 115–7
1	1·33 ± 0·02	1·155 ± 0·01
1·74	1·32 ± 0·02	1·155 ± 0·01
7·80	1·31 ± 0·02	1·158 ± 0·01

---

* Since the above was written a less accurate measurement of the $L\alpha_1 : L\beta_1$ ratio has been determined. It is 100 : 40. Corrections for absorption etc. (see p. 188) tend to balance out and were within the limits of experimental error, which was 10 per cent.

Thus within the limits of experimental error it is justifiable to assume the validity of the reciprocity law.

In conclusion I wish to express my gratitude to Professor Laby for the continued assistance and encouragement received from him throughout the course of this work. My thanks are also due to Dr L. H. Martin for his helpful advice and interest.

DISCUSSION

Prof. F. L. Hopwood: I should like to congratulate the author on a sound and valuable contribution. I would also point out that although under the conditions under which the author worked it is permissible to use the photographic method for the measurement both of X-ray intensities and of wave-lengths, yet the photographic method for both types of measurement leads to erroneous results in dispersive media. Over what range does the author consider the relation

$$\text{density} \propto \text{number of quanta absorbed}$$

to be valid, as theoretical considerations would point to another law?

Miss T. J. Dillon asked the author why he had abandoned the tungsten-filament X-ray tube for one with a Wehnelt filament (p. 186 of the paper).

Author's reply: The results obtained by Berthold, as shown in the formula on p. 185, throw light on the question raised by Prof. Hopwood. The range over which the assumption that the density varies as the number of quanta is justifiable depends on the accuracy attained in the other parts of the experiment. For the present work it would be of the order of 100 X.U. The expression shows, however, that over a considerably larger range of wave-length the assumption that the density varies as the energy absorbed is justified for moderately long X-radiation.

In reply to Miss Dillon's question, I would say that in the first place it was feared that evaporation from the tungsten filament and deposition of tungsten on the anticathode might lead to errors with the method used. In the second place, the intention was to extend the method for use over a larger range of wave-lengths, in which case the presence of the carbon paper screen (p. 187) would be undesirable.

SPARK SATELLITES OF THE *Lα* LINES OF SILVER

By H. C. WEBSTER, M.Sc.

Dixon Research Scholar, Natural Philosophy Laboratory, University of Melbourne

Received December 10, 1928. *Read and discussed February* 8, 1929

ABSTRACT. The wave-lengths of four spark satellites of silver *Lα* were measured by a relative method, the results being 4134·7, 4130·5, 4125·6, 4119·0 X.U.

In films taken in connection with the preceding paper, spark satellites were observed on the hard side of the $L\alpha_1$. The distances of these lines from $L\alpha_2$ ($L\alpha_1$ could not be used, since it had been broadened too much by halation) were measured by the projection method* usually employed in this laboratory. The mean distances, in terms of divisions of the head of the screw, for three spectral images on film G 104 were as shown in the table.

Spectral image number	α_2'	α_1'	α_2''	α_1''
1	162	211	258	314
2	174	213	256	316
3	177	210	252	314
Mean	171	211	255	315

The notation for α_1' and α_1'' has been copied from that of Thoraeus† and of van der Tuuk‡. These lines are usually denoted by α_3 and α_4 respectively. The distances of the film and the principal slit from the rotation axis of the crystal were each adjusted to 10·00 ± 0·02 cm. The wave-length of silver $L\alpha_2$ being taken as 4153·82 X.U.§, and the grating space of calcite 3029·04 X.U., the wave-lengths come out as

α_2'	4134·7 ± 0·4 X.U.
α_1'	4130·5 ± 0·2 ,,
α_2''	4125·6 ± 0·4 ,,
α_1''	4119·0 ± 0·2 ,,

---

* Eddy and Turner, *Proc. R. S.* A, **111**, 117 (1926).

† Thoraeus, *Phil. Mag.* **2**, 1007 (1926).

‡ Van der Tuuk, *Zeits. für Phys.* **41**, 326 (1927).

§ Siegbahn, *The Spectroscopy of X-Rays*, p. 118.

Previous values for α_1' and α_1'' are

α_1'	(Siegbahn's laboratory*)	4131·7 X.U.
α_1''	(Coster†)	4119·4 ,,

Careful examination of tables of wave-lengths was made to make sure that none of these lines could have proceeded from other elements present as impurities in the anticathode. The decreasing order of intensities of the lines is α_1', α_1'', α_2'', α_2'.

---

* Siegbahn, *The Spectroscopy of X-Rays*, p. 118.

† Coster, *Phil. Mag.* **43**, 1070 (1922).

THE CONSTRUCTION AND CALIBRATION OF A SENSITIVE FORM OF PIRANI GAUGE FOR THE MEASUREMENT OF HIGH VACUA

By L. F. STANLEY, A.R.C.S., B.Sc.

Research Student of the Royal College of Science

Received October 30, 1928. *Read and discussed February* 22, 1929

ABSTRACT. The low-pressure gauge here described consists of a manometer and a compensator of identical construction placed in the opposite arms of a Callendar-Griffiths bridge. Each comprises, essentially, a loop of 10 cm. of platinum wire, 0·001 in. in diameter, together with a compensating loop of 2 cm. of the same wire. The symmetry of the circuit makes errors due to thermo-electric effects very small. Investigations have been carried out to ascertain how the sensitivity of the instrument depends upon (1) the diameter of the gauge; (2) the temperature of the wire; (3) the temperature of the external walls; (4) the nature of the material of the external walls. The gauge follows variations of pressure with considerable rapidity, and its range of measurement is from 2×10^{-3} mm. to 4×10^{-6} mm. approximately.

---

§ 1. LOW-PRESSURE MEASUREMENT

This work was carried out with the view of producing an instrument capable of measuring the lowest pressures. The instrument very commonly used for measuring pressures less than 1 mm. of mercury is the McLeod gauge. This type of gauge has marked defects, one of the chief being that the reading is that of the partial pressures due to gases, and not the total pressure of gases and vapours; the readings, however, are absolute.

There are, besides, a number of types of low-pressure gauge: the type with which this paper deals is usually known as the Pirani gauge.

The Pirani gauge

The Pirani gauge* makes use of the fact that, at low pressures, the conductivity of a gas is a function of its pressure, and hence the heat dissipated by a suitable source of heat will vary when the pressure is varied. The gauge of Pirani consisted of a tantalum lamp, the wire being heated by an electric current. The resistance

* Pirani, *Ver. d. Deutsch. Phys. Ges.* **8**, 24 (1906).

of the gauge was measured by a Callendar-Griffiths bridge; a similar lamp, which had been exhausted and sealed off at a low pressure, was placed in the other arm of the bridge to compensate for variations in the air temperature.

C. F. Hale*, and later, N. R. Campbell†, have made improvements upon the gauge of Pirani.

§ 2. METHOD AND APPARATUS

To obtain a sensitive instrument it is first necessary to investigate the conditions which affect its sensitivity, and then to adjust these conditions so as to obtain a maximum sensitivity. Pirani‡ has shown that the method of calibration giving the greatest sensitivity is that of measuring the change of resistance as a function of the change of pressure, the current being kept constant. The sensitivity of the manometer will be increased by conditions that will tend to make the dissipation of heat by conduction through the gas larger, in comparison with the heat lost by direct radiation and by conduction along the supports. To make the latter loss as small as possible, "anchoring" of the wire was avoided by the use of a short loop only of the wire. In the first instance, this loop consisted of 2·5 cm. of 0·001 in. platinum wire. Its ends were soldered with gold to two thicker leads of platinum wire, which were fused into a glass tube and welded to thick copper leads. The tube was fused at its upper end into a wider tube, so that the latter enclosed the fine wire. The leads were insulated by purified asbestos wool. A similar instrument was prepared, and this was used as a compensator.

Preparation of the compensator

The purpose of the compensator was to minimize errors due to any variations in the external conditions, and it was exhausted, sealed off and placed in the arm of the bridge opposite to that occupied by the manometer. To exhaust the compensator its side tube was partly constricted and then connected by means of glass-tubing to a McLeod gauge and to a Gaede mercury rotary pump. A U-tube, a charcoal-pocket and a drying tube containing P_2O_5 were inserted between the compensator and the pump. The connections were all-glass, and the tubing was kept as wide and as short as possible. Two taps were placed between the apparatus and the pump. The compensator was exhausted by the pump and at the same time heated by an electric furnace to about 275° C.; the wire was heated to a somewhat higher temperature of 300° C. approximately. The heating was maintained and the pumps kept in operation for several days, to out-gas the instrument thoroughly; the temperature of the heater was finally reduced gradually, liquid air was continuously applied to the charcoal-pocket, and the compensator was then sealed off.

---

* C. F. Hale, *Trans. Am. Electrochem. Soc.* **20**, 243 (1911).

† N. R. Campbell, *Proc. Phys. Soc.* **33**, 287 (1921).

‡ Pirani, *loc. cit.*

The manometer was connected to the apparatus in place of the compensator and heated in the same way as the latter with the pumps working. Fig. 1 illustrates the manner in which the apparatus was connected.

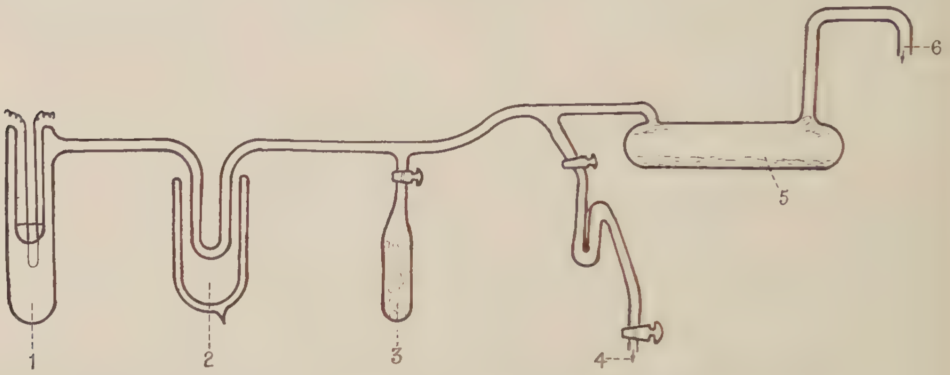


Fig. 1. Construction of apparatus: 1, gauge; 2, liquid air; 3, charcoal-pocket; 4, pump attachment; 5, P_2O_5 tube; 6, McLeod gauge attachment.

The electrical connections

The manometer and compensator were placed in the opposite arms of a Callendar-Griffiths bridge, the connections being made through mercury cups. The arrangement of the electrical circuit is represented in Fig. 2. *RR* are the ratio arms of the bridge, *TT* the bridge-coils, *MM* the manometer and compensator, G_1 a galvanometer for indicating the point of balance on the bridge, and *B* a two-volt

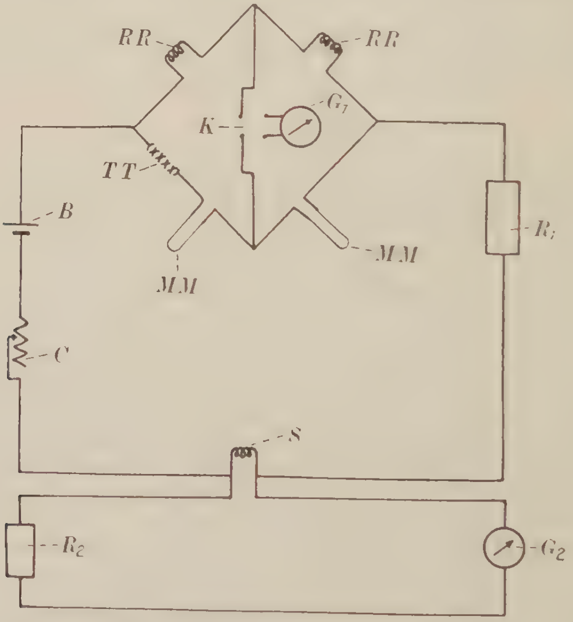


Fig. 2. Electrical connections.

accumulator connected in series with a carbon rheostat C, a 0·1 ohm resistance S, and a resistance box R_1 containing multiples and sub-multiples of the ohm. In parallel with S are connected a resistance box R_2 and a moving coil galvanometer G_2 of high sensitivity. The current was kept constant by the carbon rheostat C, a very sensitive control being obtained when the carbons were tightly packed. The galvanometer G_2 served to indicate the constancy of the current.

§ 3. EXPERIMENTAL INVESTIGATION OF THE SENSITIVITY OF THE INSTRUMENT

Experiments were carried out in order to determine in what manner the sensitivity of the gauge was affected by:

1. The diameter of the gauge.
2. The temperature of the exterior walls of the manometer.
3. The temperature of the loop itself.
4. The nature of the material of the external walls.

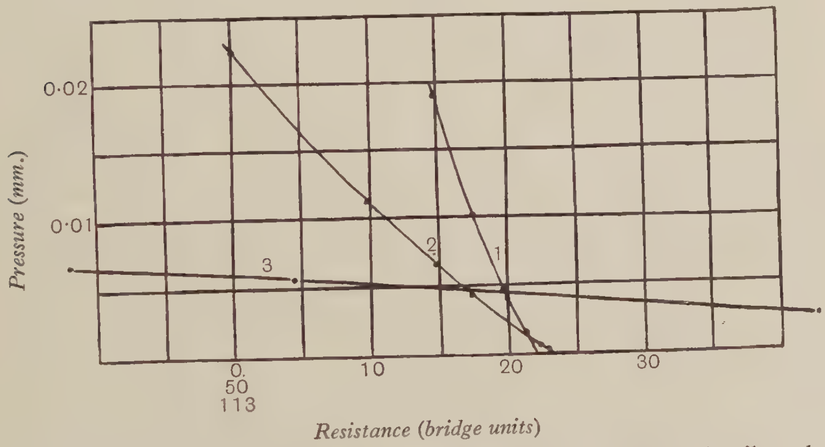


Fig. 3. Resistance-pressure curves for glass gauge No. 1, with external walls at the temperatures of (1) steam, (2) melting ice, (3) liquid air.

To investigate the first condition two sets of instruments were made, the first being 2·7 cm. in diameter and the second 1·7 cm. When readings were being taken the manometer and the compensator were immersed in melting ice, the loops were heated by a constant current sufficient to raise their temperatures to 90° C. at the lowest pressures, and the U-tube was immersed in liquid air in order to free the manometer from the presence of mercury vapour. The system was exhausted to about 0·01 mm., the taps were turned, and the point of balance was determined on the bridge, the pressure being simultaneously determined as accurately as possible by the McLeod gauge. In this way a series of readings of the bridge resistance and the corresponding pressure down to the lowest pressures were obtained. The pressures were plotted as ordinates against the corresponding readings of the bridge as abscissae. The curves obtained indicated that, at low pressures, the diameter of the tubes, when of the order mentioned above, has no effect on the sensitivity of the instrument. One might expect this from the fact that, at pressures below 0·001 mm., the mean free path of most gases is greater than 10 cm.

The chief factor controlling the sensitivity of the gauge is, undoubtedly, the second one, namely, the temperature of the external walls of the gauge. This fact is indicated by Fig. 3, in which are plotted graphs of pressure against bridge resistance, the exterior walls of the manometer and compensator being at the temperatures of (1) steam, (2) melting ice, and (3) liquid air. These graphs show clearly that the lower the external temperature of the manometer and compensator, the more sensitive is the instrument to variations of pressure. This is the result of the fact that, when the pressure is lowered, the change in the rate of dissipation of heat will be the greater, the lower the temperature of the walls of the manometer.

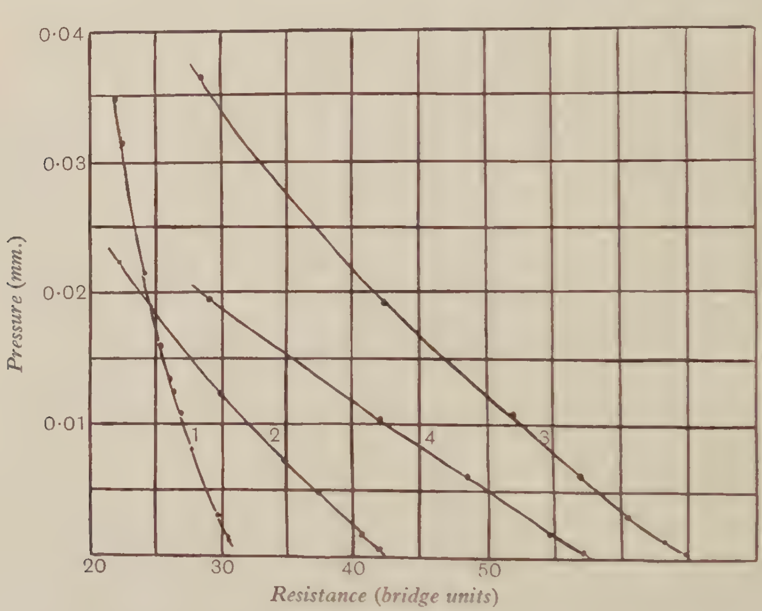


Fig. 4. Resistance-pressure curves for glass gauge No. 1, with wire at temperatures (1) 30° C., (2) 100° C., (3) 130° C., (4) 160° C.

Fig. 4 illustrates the manner in which the third condition, namely, the temperature of the wire, affects the sensitivity of the gauge. There are four graphs, the temperatures of the filament being 30, 100, 130 and 160° C. respectively. The less the slope of the graph, the greater the sensitivity of the gauge. Little increase in sensitivity is obtained by heating the wire above 100° C., as is shown in Table 1, whereas an increase in possible sources of error, such as those due to fluctuations in the heat loss along the leads, is likely to occur at such temperatures.

Table 1. Relation between sensitivity and temperature of filament

Temperature ° C.	Slope of graphs, Fig. 4 (mm. per cm. of bridge wire)
30	0·0017
100	0·0009
130	0·0007
160	0·0006

Effect of metal walls on the sensitivity of the instrument

In order to ascertain the manner in which the thermal conductivity of the external walls might affect the sensitivity of the instrument, a gauge having its walls of metal instead of glass was constructed. A solid rod of brass was turned into the form of a hollow cylinder and flanged at the top. A glass manometer, similar to one of those already calibrated, was constructed with the exception of the lower half of the external tube; the brass cylinder was turned to take the place of the latter, and a sealing-wax joint was made, the flange serving to ensure that the joint was air-tight.

The instrument was calibrated, the temperature of the filament being raised to 55° C. approximately. The graph (*B*), Fig. 7, indicates that the instrument was but slightly more sensitive than the glass one. Such a metal instrument, however, gave rise to great difficulty owing to the continuous evolution of gas from its walls and the impossibility of keeping the compensator sealed off at a low pressure. The sensitivity of the metal gauge was deemed insufficient to warrant the construction of a gauge of gas-free metal.

§ 4. MODIFICATION OF THE INITIAL FORM OF THE GAUGE

As the resistance of the form of the gauge already described changed by a small value only when the pressure was reduced to the lowest values, the gauge was modified by increasing the length of the loop to 10 cm. A loop longer than this would not be convenient unless anchored in some way. To minimize still further the errors due to fluctuations in heat loss along the leads, duplicate pairs of leads were inserted in the compensator and the manometer, and each pair was connected by 2 cm. of wire cut from the same reel as the longer loops. The short loop of the manometer was placed in the arm of the bridge containing the longer loop of the compensator, and *vice versa*. The presence of thermo-electric effects cannot, in this case, be eliminated by reversing the current through the resistance to be measured, as the point of balance would thereby be lost. The method adopted, therefore, was to obtain symmetry in the bridge circuit by adjusting the resistances of the manometer and compensator to equality within 0·1 per cent. This was effected first by adjusting the length of the wire and finally by stretching the wire. The manometer is illustrated in Fig. 5.

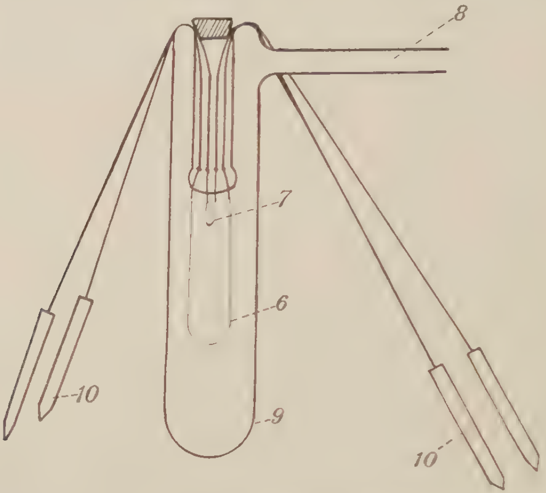


Fig. 5. Construction of modified form of gauge. 6, loop of 10 cm. of 0·001 in. platinum wire; 7, compensating loop of 2 cm. of identical wire; 8, tube for connection to pressure system; 9, glass tube 2·7 cm. diameter; 10, leads for connection to bridge.

The calibration

The compensator was connected to the system previously described and sealed off at a pressure of 0·00018 mm. in the manner indicated. The manometer was then fused in place of the compensator and out-gassed. To maintain the external temperature of the walls as constant as possible, the gauge was immersed in a tank containing ice and water which could be thoroughly stirred, a constant stream of ice-cold water being sent past the gauge.

In the first calibration the filament was heated, at the lowest pressures, to a temperature of 23° C. only, by a constant current of 0·008835 amp. in the main circuit. Fig. 6 gives the calibration curve. The slope of the graph at the lowest pressures indicates that 1 mm. shift along the bridge wire corresponds to a change of pressure of 8×10^{-6} mm.

§ 5. NOTE ON THE ACCURACY OF THE ORDINARY TYPE OF McLEOD GAUGE

In Fig. 6 curve (*b*) is similar to curve (*a*), identical readings being plotted on a magnified scale; in (*b*) all the readings do not lie on the calibration curve, and this fact was attributed primarily to inaccuracies in the reading of the McLeod gauge. On the assumption that the calibration curve (*b*) was correct, the mean error in the readings of the pressure taken with this McLeod gauge between 10^{-3} mm. and 10^{-4} mm. was 4·5 per cent.

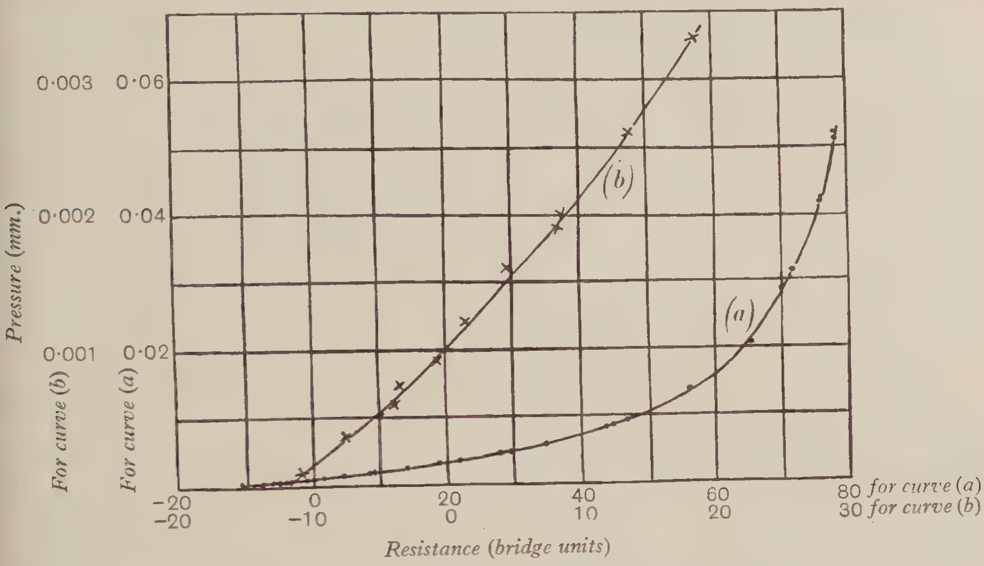


Fig. 6. Pressure-resistance curves for glass gauge No. 2.

The Dunoyer-McLeod gauge

A design of McLeod gauge due to M. Dunoyer was acquired with the view of making a more accurate calibration. This gauge is, in effect, a compound form of the original type, and proved very satisfactory for the measurement of low pressures. With this gauge the Pirani gauge was re-calibrated. The current through the main circuit was kept constant at 0·01591 amp., the temperature of the wire being thereby raised to 55° C. at the lowest pressures. The readings plotted were obtained over a course of a week or two, and they all fall very closely on the calibration curve (*A*), Fig. 7.

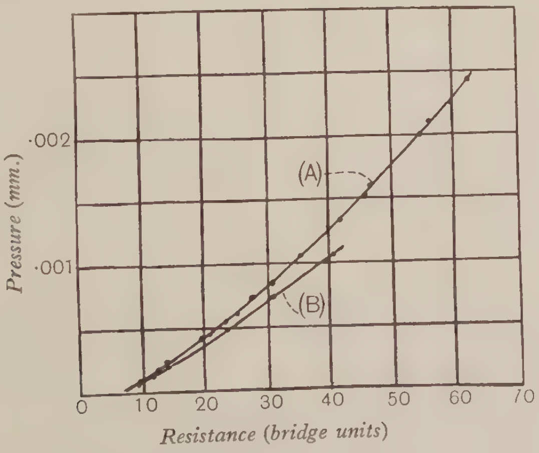


Fig. 7. Pressure-resistance curves for (*A*) glass gauge No. 2, and (*B*) metal gauge.

Provided the pressure in the system was steady, readings could be repeated to agree to 1 mm.; it was found that the change of pressure corresponding to 1 mm. shift along the bridge wire was, at the lowest pressures, $3{\cdot}4 \times 10^{-6}$ mm. The instrument is, therefore, suitable for measuring changes of pressure of this order at low pressures. Figs. 6 and 7 indicate that even at the lowest pressures "a straight-line law" of the variation of pressure with resistance does not appear to be followed accurately, under the relevant conditions of the measurement of pressure and of resistance. The change of the slope of the graph, however, for pressures less than 5×10^{-4} mm. is very small.

§ 6. CONCLUSIONS

The low-pressure gauge described can be constructed fairly easily, and it will follow moderately rapid variations of pressure; the limit to the speed of measurement is governed by the time necessary to obtain a point of balance on the bridge wire.

The instrument is capable of measuring pressures within the range between 2×10^{-3} mm. and 4×10^{-6} mm. It is not particularly suitable for rough-and-ready measurements of pressure, as a certain amount of care is required in its use. It might, however, be useful when the value of the pressure needs to be known as accurately as possible, as is the case in some scientific researches.

In conclusion, I have to thank Miss M. Bell, B.Sc., D.I.C., for useful advice on the production of high vacua, and also Professor H. L. Callendar, F.R.S., for advice on the method of procedure.

DISCUSSION

Miss T. J. DILLON: Would the author kindly say (1) what gas was introduced into the tube to produce the increase of pressure; (2) what method was used for finding the temperature of the filament; (3) whether the sensitivity of the gauge was studied at any high temperatures?

Mr L. C. JESTY: I should like to ask the author his reasons for baking his comparison gauge for several days at such a low temperature as 275°. Soft glass bulbs will stand a temperature of 400°–450° when evacuated, and therefore I consider that baking for an hour or even less at 400° would have degassed the glass more efficiently.

Prof. C. H. LEES: It would be of interest if Mr Stanley would say what influence the size of the vessel containing the filament has on the constant of the instrument.

AUTHOR'S reply: The gas used in the calibration of the instrument was dry air, freed from CO_2. To measure the temperature of the filament the gauge was used as a platinum thermometer, its fundamental interval being determined by finding its resistance at 0° C. and at 100° C. The comparative instability of the gauge, together with the fact that at high temperatures a considerable amount of the heat is lost by radiation at a rate independent of the pressure, were the reasons why the filament was not raised to higher temperatures.

It has been shown that soda glass evolves gas in two well-defined stages, one below 300° C., the other above this temperature*. It is concluded that the products removed below 300° C. are adsorbed gases, while at higher temperatures there is an actual decomposition of the glass itself. As the walls of the gauge do not experience temperatures above room temperature, it is sufficient to remove the adsorbed gases only.

The sensitivity of the gauge is independent of the diameter of the instrument at low pressures, provided that the diameter be less than the mean free path of the molecules. At pressures below 0·001 mm., the mean free path in most gases is greater than 10 cm.

---

* R. G. Sherwood and J. E. Shrader, *Journ. Am. Chem. Soc.* **40** (1918).

THE FREE PERIODS OF A COMPOSITE ELASTIC COLUMN OR COMPOSITE STRETCHED WIRE

By CHARLES H. LEES, D.Sc., F.R.S.

Received January 17, 1929. *Read and discussed February* 22, 1929

ABSTRACT. The free periods of the longitudinal oscillations of an elastic column, one portion of which has different elastic properties from the remainder, are determined for different positions of the junction when both ends of the column are nodes, when one is an antinode, and when both are antinodes. A graphical method of dealing with the problems is developed. Observations in the case of a composite stretched wire agree with the theoretical results.

§ 1. INTRODUCTION

Some investigations which are being carried out at the Safety in Mines Research Stations at Sheffield and at Buxton have rendered it desirable that the possible oscillations of a column of gas, one portion of which is at a temperature T_1 and the other at a temperature T_2, should be investigated in the three possible cases, i.e. when the column is closed at each end, when one end is open and when both ends are open to the atmosphere.

For displacements which are not too large, the problem of the longitudinal oscillations of an elastic column of a single material and that of the transverse oscillations of a thin stretched wire of a single material lead to the same differential equation, and the end conditions for a column of gas closed at each end or of a rod clamped at each end are identical with those for a wire stretched between fixed supports.

The problem of the reflection which a sudden change of linear density produces in the case of a progressive wave travelling along a composite stretched wire has been considered by Rayleigh*, but the case of standing waves does not appear to have been treated. In the case of a composite column of gas or a composite stretched wire the change is generally in the mass per unit length only, the adiabatic elasticity in the case of the gas and the stretching force in the case of the wire remaining constant. The free periods of a given length of composite column or wire then lie between those of the same length when composed entirely of one or other of the two constituent gases or wires. But the effect on the periods of a small change of position of the junction of the two constituents is small when the junction is near a node, since the motion there is small, and large when it is near an antinode where the motion is large. The relation between the frequency and the position of the junction cannot therefore be a linear one.

When the composite column consists of two gases with different values of γ, the ratio of the specific heats at constant pressure and at constant volume, or of two liquids or solids with different adiabatic elasticities, the relation between the frequency and position of the junction is less simple and the frequency may not in all cases lie between those of the same length of the constituents.

---

* *Sound*, Vol. 1, Section 148 *a* (1896).

§ 2. BOTH ENDS NODES

To deal with the general case, in which at the junction of the two constituents changes of both elasticity and density may occur, take the x axis along the axis of the column, let x be the undisplaced position of a point and ξ its displacement forward along the x axis in the case of longitudinal oscillations, or at right angles to the x axis in the case of transverse oscillations, at the time t.

Then the equation $\partial^2\xi_1/\partial t^2 = (F_1/m_1)\,\partial^2\xi_1/\partial x^2$

holds for each point of the first constituent and the equation

$$\partial^2\xi_2/\partial t^2 = (F_2/m_2)\,\partial^2\xi_2/\partial x^2 \qquad \ldots\ldots(2{\cdot}1)$$

for each point of the second, where F_1, F_2 are the moduli of adiabatic elasticity for the longitudinal displacements in the column or the stretching force in the wire, and m_1, m_2 the masses per unit volume in the column or per unit length in the wire*.

The solutions of these equations are

$$\xi_1 = a_1 \sin\{2\pi n\, x/\sqrt{(F_1/m_1)}\} \cos 2\pi nt$$

and

$$\xi_2 = a_2 \sin\{2\pi n\,(L-x)/\sqrt{(F_2/m_2)}\} \cos 2\pi nt \qquad \ldots\ldots(2{\cdot}2),$$

where the time is reckoned from the instant when the displacements have their maximum values, L is the total length of the column or wire, n the frequency of the oscillation and a_1 and a_2 are constants.

If n_1 be the fundamental frequency when the whole length is occupied by the first constituent and n_2 when by the second, we have

$$2\pi n_1 L/\sqrt{(F_1/m_1)} = \pi \text{ and } 2\pi n_2 L/\sqrt{(F_2/m_2)} = \pi.$$

Hence the equations may be written

$$\xi_1 = a_1 \sin(\pi\, nx/n_1L) \cos 2\pi nt$$

and

$$\xi_2 = a_2 \sin[\pi\, n\,(L-x)/n_2L] \cos 2\pi nt \qquad \ldots\ldots(2{\cdot}3).$$

If l_1 be the distance of the junction of the two constituents from the origin, we must have at $x = l_1$ the displacements identical and the forces transmitted through the junction identical. That is at $x = l_1$, $\xi_1 = \xi_2$ and $F_1\,(\partial\xi_1/\partial x) = F_2\,(\partial\xi_2/\partial x)$.

Hence $$a_1 \sin(\pi\, nl_1/n_1L) = a_2 \sin\{\pi\, n\,(L-l_1)/n_2L\}$$

and $$F_1\,(a_1/n_1)\cos(\pi\, nl_1/n_1L) = -\,F_2\,(a_2/n_2)\cos\{\pi\, n\,(L-l_1)/n_2L\}.$$

Thus the frequency n is subject to the condition

$$(n_1/F_1)\tan(\pi\, nl_1/n_1L) = -\,(n_2/F_2)\tan\{\pi\, n\,(L-l_1)/n_2L\} \qquad \ldots\ldots(2{\cdot}4).$$

Let $nl_1 = n_1Lp_1$ and $n\,(L-l_1) = n_2Lp_2$, where p_1 and p_2 are constants. The equation becomes

$$(n_1/F_1)\tan p_1\pi = -\,(n_2/F_2)\tan p_2\pi \qquad \ldots\ldots(2{\cdot}5).$$

---

* Rayleigh, *Sound*, Vol. 1, Sections 122 and 152; Vol. 2, Section 249 (1896).

For any assigned value of p_1 this equation allows the corresponding value of p_2 to be calculated; then the equation

$$n = p_1 n_1 + p_2 n_2 \qquad \text{......(2·6)}$$

gives the frequency n, and

$$l_1/L = p_1 n_1/n \qquad \text{......(2·7)}$$

the position l_1 of the junction of the two constituents. The series of possible angles for the same value of the tangent gives the frequencies of the fundamental and of the harmonics. It is therefore only necessary to calculate p_2 for a few assigned values of p_1 between 0 and 1, to allow the curve connecting the frequency with the position of the junction to be drawn for both fundamental and harmonics.

For the fundamental, while p_1 varies from 0 to 0·5 and to 1, p_2 varies from 1 to 0·5 and 0, giving at these values $n = n_1$, $(n_1 + n_2)/2$ and n_2 respectively, and $l_1/L = 0$, $n_1/(n_1 + n_2)$ and 1 respectively.

For the first harmonic, while p_1 varies from 0 to 0·5, 1·0, 1·5 and 2, p_2 varies from 2 to 1·5, 1·0, 0·5 and 0, giving at these values $n = 2n_2$, $0{\cdot}5n_1 + 1{\cdot}5n_2$, $n_1 + n_2$, $1{\cdot}5n_1 + 0{\cdot}5n_2$ and $2n_1$ respectively, and $l_1/L = 0$, $n_1/(n_1 + 3n_2)$, $n_1/(n_1 + n_2)$, $3n_1/(3n_1 + n_2)$ and 1·0 respectively.

For the second harmonic p_1 varies from 0 to 3 and p_2 from 3 to 0 with corresponding values for n and l_1/L.

If x is at a node in the first constituent, equation (2·3) shows that

$$x/L = \text{integral multiple of } n_1/n,$$

and if it is at an antinode

$$x/L = \text{half an odd integral multiple of } n_1/n.$$

If it is at a node in the second

$$(L - x)/L = \text{integral multiple of } n_2/n,$$

and if at an antinode

$$(L - x)/L = \text{half an odd integral multiple of } n_2/n \qquad \text{......(2·8).}$$

The junction itself is therefore a node if p_1 in $l_1/L = p_1 n_1/n$ is an integer, and is an antinode if p_1 is half an odd integer ......(2·9).

§ 3. VARIATION OF FREQUENCY

To determine whether the frequency reaches a maximum or minimum for any position of the junction we differentiate the equation for n, (2·6), and the equation for p_1 and p_2, (2·5), and on eliminating dp_1 and dp_2 we get

$$(n_2 . n_1/F_1) \sec^2 p_1\pi = (n_1 . n_2/F_2) \sec^2 p_2\pi$$

or

$$F_1 \cos^2 p_1\pi = F_2 \cos^2 p_2\pi$$

as the condition for the frequency to be a maximum or a minimum. Substituting tangents and eliminating $\tan p_2$, by help of equation (2·5) we get

$$\tan^2 p_1\pi = \{(F_1/F_2)^2 - (F_1/F_2)\}/\{(F_1/F_2) - (n_1/n_2)^2\} = \{(F_1/F_2) - 1\}/\{1 - (m_2/m_1)\}$$

and $$\tan^2 p_2\pi = \{1 - (F_2/F_1)\}/\{(m_1/m_2) - 1\} \qquad \text{......(3·1)},$$

which determine p_1 and p_2 and hence l_1 for a maximum or minimum n.

Hence, for the frequency to have a maximum or a minimum, F_1/F_2 must lie between 1 and $(n_1F_2/n_2F_1)^2$ or 1 must lie between F_1/F_2 and m_2/m_1.

If F_1 be equal to F_2, as it will if we are dealing with a composite stretched wire or a column of gas at constant pressure with γ the same for each constituent, or with any column in which each constituent has the same adiabatic elasticity, $\tan^2 p_1\pi = 0$ and for the maximum n of the fundamental the junction lies at one end, for the minimum at the other end of the wire.

§ 4. GRAPHICAL SOLUTION

The required solutions of the conditional equation (2·5) may be obtained and the relations between the quantities which enter into the problem readily seen from the following graphical construction.

From the point A of a horizontal line mark off in opposite directions AC_1 and AC_2 equal on some convenient scale to the fundamental frequencies n_1 and n_2 respectively, and with centres C_1 and C_2 and radii C_1A, C_2A respectively, describe two circles cutting the horizontal in A_1 and A_2; these circles we may call "the n_1 and n_2 circles." Find the position of the point B such that $C_1B : BC_2 :: n_1/F_1 : n_2/F_2$ and through B draw the vertical BPQ. Join P to C_1 and C_2 and produce each if necessary to cut the circumference of the n_1 circle in P_1, P_1' and the n_2 circle in P_2P_2', P_1 and P_2 being the points nearest to A at which the circles are cut. Then P_1C_1A and $P_2C_2A_2$ are the principal values of the angles $p_1\pi$ and $p_2\pi$ of the conditional equation (2·5), and other values are obtained by adding integral multiples of π to the principal values. The arc AP_1 of the n_1 circle is $n_1p_1\pi$ and the arc A_2P_2 of the n_2 circle is $n_2p_2\pi$. Hence $n\pi =$ (arc AP_1 + arc A_2P_2) and the position of the junction is given by $l_1/L =$ arc AP_1/(arc AP_1 + arc A_2P_2). As P moves along

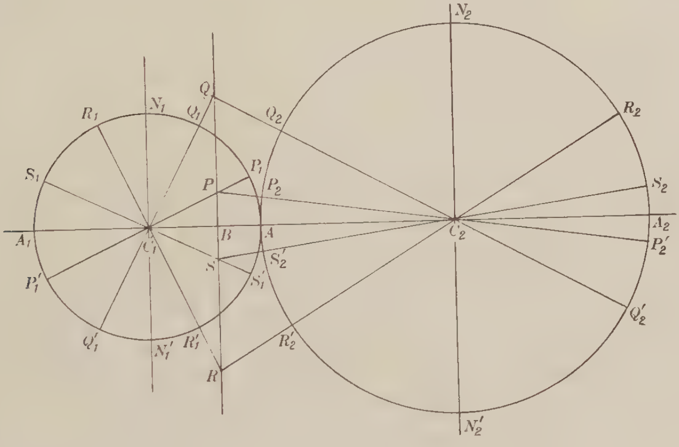


Fig. 1. $P_1C_1A = p_1\pi$, $P_2C_2A_2 = p_2\pi$, $n\pi = AP_1 + A_2P_2$, $l_1/L = AP_1/(AP_1 + A_2P_2)$.

BPQ to Q we get the arcs AQ_1, A_2Q_2 etc. and when it reaches $-\infty$ the arcs AN_1 and A_2N_2 subtend angles of $\pi/2$ at C_1 and C_2. Hence the corresponding frequency n is the mean of n_1 and n_2, and the junction is at a point l_1 such that $l_1/L = n_1/(n_1 + n_2)$. The point P now moves to $-\infty$ and approaches B from below. If R be one of its positions the arcs are now AR_1 and A_2R_2, which as R approaches B become π and 0 respectively.

For the positions of the nodes and antinodes for any values of p_1 and p_2 which satisfy (2·5) we use the relations (2·8).

The relations (2·9) show that for the fundamental the junction is an antinode for $p_1 = 0{\cdot}5$ and therefore for $l_1/L = n_1/(n_1 + n_2)$, and for the first harmonic the junction is an antinode for $p_1 = 0{\cdot}5$ and $1{\cdot}5$ and therefore for $l_1/L = n_1/(n_1 + 3n_2)$ and $3n_1/(3n_1 + n_2)$, and a node for $p_1 = 1{\cdot}0$ and therefore for $l_1/L = n_1/(n_1 + n_2)$.

Fig. 1 has been drawn to illustrate the case in which n for the fundamental has a maximum value greater than n_2, the higher of the two constituent frequencies, and a minimum less than n_1, the lower, and corresponding maxima and minima for the harmonics.

If B in the figure coincide with A the maximum for the fundamental is at n_2 and the minimum at n_1, the rates of change of n being zero at these points.

If B move to the other side of A there are no maxima or minima, the condition of section 3 being no longer satisfied.

§ 5. EXPERIMENTS ON WIRES

In order to verify the above theory experimentally, two steel wires of diameters 0·021 and 0·041 cm. respectively and about a metre long were attached to each other by silver solder and stretched about 3 cm. above the bench by a weight of 1·5 kg. hanging over a pulley. Underneath the wire two knife-edge supports 50 cm. apart, attached to a lath, could be placed so that the joint came in any required position between the knife edges. Two additional knife-edge supports were placed one on each side of the former two, and were so adjusted that the three lengths of wire between the four knife edges were in unison. This result was secured by gently plucking one of the side lengths and seeing that the centre and other side lengths were both set into vibration. The resonance was only considered satisfactory when either side length when plucked would set the other lengths into vibration. The side lengths and the distance of the junction from one knife edge were then measured. From the side lengths the frequency was calculated, the lengths to give a frequency of 256 having been found previously to be for the thick wire 25·7 cm., and for the thin 49·7 cm. It was found advantageous to place a light knife edge on the top of the wire at the point where it passed over each lower knife edge.

The curves of Fig. 2 show the relation found between the position of the joint and the frequency of the vibration. The observed* values agree very closely with the calculated ones.

---

* I have to thank Mr D. J. Fewings, one of my senior students, for taking these observations.

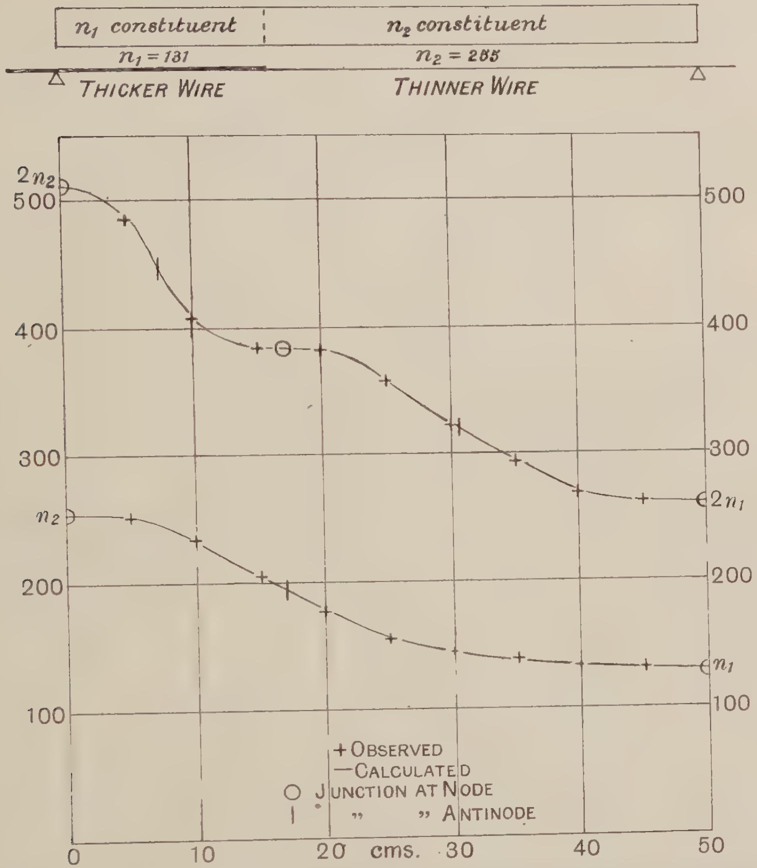


Fig. 2. Frequencies of composite column, with a node at each end, for different positions of junction.

Table 1, which has been calculated for the two wires, shows how readily the solutions of the conditional equation (2·5) may be written down after the first pair of values of p_1 and p_2 have been calculated.

§ 6. ONE END AN ANTINODE

When one end only of the column is a node the other an antinode, as in a resonance tube closed at the bottom and containing a gas denser than air* in its lower part, the solutions of the differential equations of § 2 become

$$\xi_1 = a_1 \sin \{2\pi n\, x/\sqrt{(F_1/m_1)}\} \cos 2\pi nt$$

and

$$\xi_2 = a_2 \cos \{2\pi n\, (L - x)/\sqrt{(F_2/m_2)}\} \cos 2\pi nt \qquad \text{......(6·1)},$$

L being the length of the column, or in the case of a gas column the length plus the correction for the open end which is approximately 0·3 times the diameter of the column.

---

* So long as the open end of the tube is an antinode the gas in the upper part of the tube need not be air.

If n_1 is the frequency of vibration of the column when composed entirely of the first constituent and n_2 when composed entirely of the second constituent we have

$$2\pi n_1 (L/\sqrt{F_1/m_1}) = \pi/2 \text{ and } 2\pi n_2 (L/\sqrt{F_2/m_2}) = \pi/2.$$

Hence the equations for the displacements may be written

$$\xi_1 = a_1 \sin \{(\pi/2)\, nx/n_1 L\} \cos 2\pi nt$$

and

$$\xi_2 = a_2 \cos [(\pi/2)\, n (L - x)/n_2 L] \cos 2\pi nt \qquad \ldots\ldots(6{\cdot}2).$$

Table 1. Composite wire of Fig. 2

Case for which $n_1 = 131$, $n_2 = 255$, $\tan p_2\pi = -(n_1/n_2)$, $\tan p_1\pi = -0{\cdot}514 \tan p_1\pi$.

p_1	$p_1\pi$	$\tan p_1\pi$	$\tan p_2\pi$	$p_2\pi$	p_2	$p_1 n_1$	$p_2 n_2$	n	l_1/L
	Fundamental, p_1 and p_2 between 0 and 1								
0·0	0°	0·0	0·0	180·0°	1·0	0	255	255	0·0
0·2	36	0·727	− 0·374	159·5	0·886	26	226	252	0·103
0·4	72	3·078	− 1·582	122·3	0·679	52	173	225	0·231
0·5	90	∞	∞	90·0	0·500	66	127	193	0·339
0·6	108	− 3·078	1·582	57·7	0·321	79	82	161	0·491
0·8	144	− 0·727	0·374	20·5	0·114	105	29	134	0·784
1·0	180	0·0	0·0	0·0	0·0	131	0	131	1·0
	First harmonic, p_1 and p_2 between 0 and 2								
0·0	0°	0·0	0·0	360·0°	2·0	0	510	510	0·0
0·2	36	0·727	− 0·374	330·5	1·886	26	481	507	0·051
0·4	72	3·078	− 1·582	302·3	1·679	52	428	480	0·108
0·5	90	∞	∞	270·1	1·500	66	382	448	0·147
0·6	108	− 3·078	1·582	237·7	1·321	79	337	416	0·190
0·8	144	− 0·727	0·374	200·5	1·114	105	284	389	0·270
1·0	180	0·0	0·0	180·0	1·0	131	255	386	0·339
1·2	216	0·727	− 0·374	159·5	0·886	157	226	383	0·410
1·4	252	3·078	− 1·582	122·3	0·679	183	173	356	0·514
1·5	270	∞	∞	90·0	0·500	197	127	324	0·606
1·6	288	− 3·078	1·582	57·7	0·321	210	82	292	0·719
1·8	324	− 0·727	0·374	20·5	0·114	236	29	265	0·891
2·0	360	0·0	0·0	0·0	0·0	262	0	262	1·0

At the junction of the two constituents, $x = l_1$, we have as before

$$\xi_1 = \xi_2 \text{ and } F_1 (\partial\xi_1/\partial x) = F_2 (\partial\xi_2/\partial x).$$

Hence

$$a_1 \sin \{(\pi/2)\, nl_1/n_1 L\} = a_2 \cos \{(\pi/2)\, n (L - l_1)/n_2 L\}$$

and

$$F_1 (a_1/n_1) \cos \{(\pi/2)\, nl_1/n_1 L\} = F_2 (a_2/n_2) \sin \{(\pi/2)\, n (L - l_1)/n_2 L\}.$$

Thus the frequency n satisfies the condition

$$(n_1/F_1) \tan \{(\pi/2)\, nl_1/n_1 L\} = (n_2/F_2) \cot \{(\pi/2)\, n (L - l_1)/n_2 L\}.$$

Writing again $nl_1 = n_1 L p_1$, $n (L - l_1) = n_2 L p_2$, where p_1 and p_2 are constants, the condition becomes

$$(n_1/F_1) \tan (p_1 \pi/2) = (n_2/F_2) \cot (p_2 \pi/2) = -(n_2/F_2) \tan \{(p_2 - 1)\, \pi/2\} \qquad \ldots\ldots(6{\cdot}3).$$

For any assigned value of p_1, p_2 may thus be calculated; then

$$n = p_1 n_1 + p_2 n_2 \text{ and } l_1/L = p_1 n_1/n$$

as before.

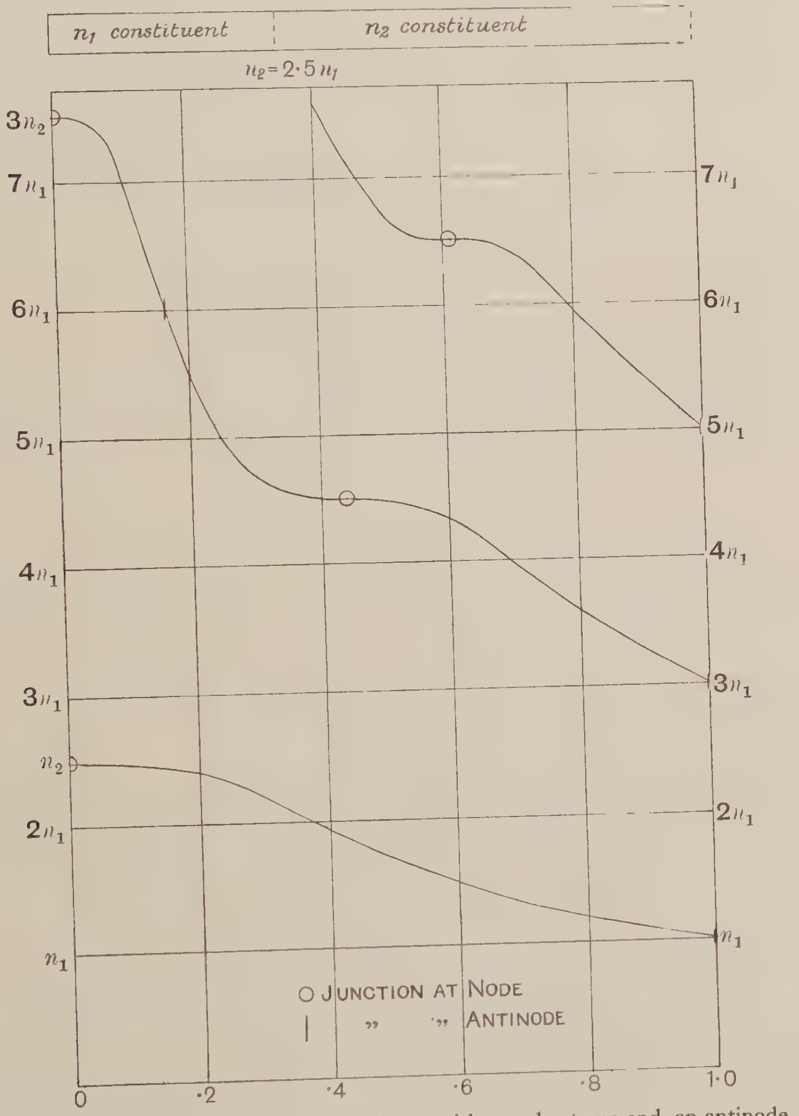


Fig. 3. Frequencies of composite column with a node at one end, an antinode at the other, for various positions of the junction.

For the fundamental, p_1 varies from 0 to 1 while $p_2 - 1$ varies from 0 to -1 and p_2 from 1 to 0. For the first harmonic p_1 varies from 0 to 1, 2 and 3, while $p_2 - 1$ varies from 2 to 1, 0 and -1, and p_2 from 3 to 2, 1 and 0.

If x is at a node in the first constituent, (6·2) shows that $x/L =$ an even multiple of n_1/n, and if at an antinode $x/L =$ an odd multiple of n_1/n.

If x is at a node in the second constituent, $(L - x)/L =$ an odd multiple of n_2/n, and if at an antinode an even multiple.

The junction between the constituents is therefore a node if p_1 in the equation $l_1/L = p_1 n_1/n$ is an even integer, and an antinode if it is an odd integer.

Fig. 3 gives the frequencies of the fundamental and harmonics in terms of the position of the junction when $F_1 = F_2$, $n_1 = 100$, $n_2 = 250$, and it applies with a suitable change of the frequency scale to any case in which $n_2/n_1 = 2{\cdot}5$.

In the graphical diagram Fig. 1, B now coincides with A and the angles P_1C_1A, P_2C_2A are now $p_1(\pi/2)$ and $(p_2 - 1)\pi/2$. For the fundamental P_1 moves from A to N_1, P_2 from A_2 to N_2. For the first harmonic P_1 moves over $AN_1A_1N_1'$, P_2 over $AN_2A_2N_2'$.

§ 7. BOTH ENDS ANTINODES

When both ends of the composite column are antinodes and L is the length of the column, or in the case of a gas column that length plus the corrections for the two ends, we have

$$\xi_1 = a_1 \cos\{2\pi n\, x/\sqrt{(F_1/m_1)}\} \cos 2\pi nt$$

and
$$\xi_2 = a_2 \cos[2\pi n\,(L - x)/\sqrt{(F_2/m_2)}] \cos 2\pi nt \qquad \ldots\ldots(7{\cdot}1).$$

If n_1 is the fundamental frequency for the column composed entirely of the first constituent and n_2 for the second,

$$2\pi n_1\{L/\sqrt{(F_1/m_1)}\} = \pi \text{ and } 2\pi n_2\{L/\sqrt{(F_2/m_2)}\} = \pi.$$

Hence
$$\xi_1 = a_1 \cos(\pi\, nx/n_1L) \cos 2\pi nt$$

and
$$\xi_2 = a_2 \cos\{\pi\, n\,(L - x)/n_2L\} \cos 2\pi nt \qquad \ldots\ldots(7{\cdot}2).$$

The conditions at the junction give

$$a_1 \cos(\pi\, nl_1/n_1L) = a_2 \cos\{\pi\, n\,(L - l_1)/n_2L\}$$

and
$$F_1(a_1/n_1) \sin(\pi\, nl_1/n_1L) = -F_2(a_2/n_2) \sin\{\pi\, n\,(L - l_1)/n_2L\}.$$

Hence
$$(n_1/F_1) \cot(\pi\, nl_1/n_1L) = -(n_2/F_2) \cot\{\pi\, n\,(L - l_1)/n_2L\}.$$

With $nl_1 = n_1Lp_1$ and $n(L - l_1) = n_2Lp_2$, this becomes

$$(n_1/F_1) \cot p_1\pi = -(n_2/F_2) \cot p_2\pi \text{ or } (F_1/n_1) \tan p_1\pi = -(F_2/n_2) \tan p_2\pi \ldots\ldots(7{\cdot}3),$$

which determines p_2 if p_1 is assigned. Then as before

$$n = p_1n_1 + p_2n_2 \text{ and } l_1/L = p_1n_1/n.$$

The method of calculating pairs of values of p_1 and p_2 which satisfy the conditional equation (7·3) is identical with that used in calculating Table 1, p. 210. The condition for maximum and minimum frequencies is that n_1/n_2 must lie between 1 and $(F_1n_2/F_2n_1)^2$. The graphical method of Fig. 1 may again be used to obtain solutions of equation (7·3) and to illustrate the variation of the free periods of the column.

DISCUSSION

Dr D. OWEN referred to the fact that the work described in the paper had originated from an investigation undertaken on behalf of the Safety in Mines Research Council. He wondered how many of those who benefited by the work of that Council would appreciate the significance of the paper if they were to read it, and how many members of the public were aware of the contributions which pure science was making to an important social service.

A CAPILLARY TUBE METHOD FOR THE SIMULTANEOUS DETERMINATION OF SURFACE TENSION AND OF DENSITY

By ALLAN FERGUSON, M.A., D.Sc., and J. A. HAKES, B.Sc.,
East London College

Received February 5, 1929. Read and discussed February 22, 1929

ABSTRACT. A capillary tube of radius r is immersed vertically to a depth h_1 in the liquid of density ρ_1 under test. The pressure $g\rho h$ required to force the meniscus down to the lower end of the capillary and to hold it there is measured. If h_1, and consequently h, be varied, a plot of ρh against $(h_1 - r\ 3)$ gives a straight line from whose slope and intercept the surface tension and the density of the liquid may be inferred.

§ 1. INTRODUCTION

Despite the many difficulties attendant on capillary rise experiments for the measurement of surface tension, the method still continues in wide use and, in some of its different forms, is the most important of the methods which provide the surface tension numbers to be found in the leading tables of constants. Some years ago it was pointed out by one of us(1) that a great many of the disadvantages attendant on the practice of the method could be swept away by the simple expedient of *forcing the meniscus down to the lower end of a vertical capillary immersed in the liquid under test and measuring, on a suitable manometer, the pressure required to hold it there.* The trouble of cleaning and calibrating the tube is thus reduced to a minimum, the temperature of the meniscus may be taken by means of a thermocouple whose junction is placed in the immediate neighbourhood of the meniscus, the radius of the tube is easily and accurately measured, and the measurement of the "capillary-rise," transferred as it is to the pressure gauge, may be considerably magnified by the use of a special form of gauge, or of a suitable light liquid in the ordinary U-tube manometer.

Measurements of surface tension by a capillary tube method are primarily concerned with the determination of a pressure and a curvature—the density of the liquid under test appears in the ordinary capillary-rise formula simply because the liquid acts as its own manometer. In the method just described the density of the test-liquid enters but incidentally and is required on account of the back-pressure, $g\rho_1 h_1$, due to the fact that the meniscus is at a depth h_1 below the free surface of the liquid. Obviously by varying h_1 it becomes possible to measure both surface tension and density.

§ 2. EXPERIMENTAL

The disposition of the apparatus employed is shown in Fig. 1, which is almost self-explanatory. The pressure is adjusted by means of the bottle shown until the lower end of the meniscus is just flush with the plane end of the tube; this setting may be repeated with very great consistency, observation of the end of the tube being made by means of a low power reading microscope. A needle point is adjusted so as just to touch the *horizontal* surface of the liquid under experiment and h_1 is obtained by measurement of the vertical distance between the needle point and the end of the tube. The pressure required to force down the meniscus is given at once from a knowledge of the difference in level between the surfaces of the liquid (aniline) in the manometer shown. These last two measurements were made with the help of a vertical-reading microscope carrying a vernier graduated to read 0·01 mm. The radius of the end of the tube was measured by means of a micrometer eyepiece, which eyepiece was standardized by two stage micrometers, one by Zeiss and one by Baker. These micrometers gave results which were in agreement to ·003 mm. The density ρ of the aniline in the manometer was determined in the usual way by the use of a pyknometer.

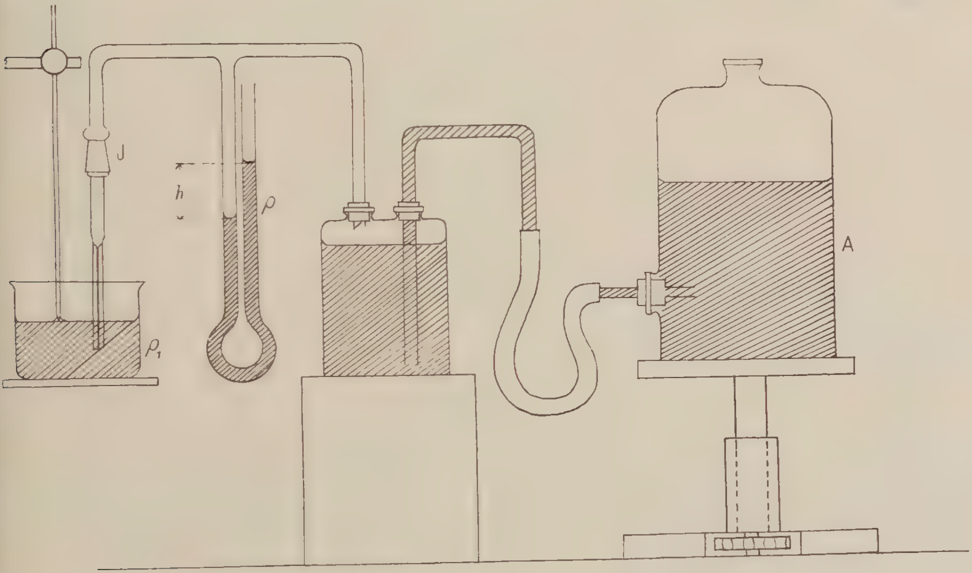


Fig. 1.

It is important that the end of the tube shall be plane and that the plane of the end shall be perpendicular to the axis of the tube. This was ensured by placing the tube in a vertical hole, slightly larger than the tube, which was bored in an iron disk shaped as shown in Fig. 2. The tube was fixed in the disk by means of fusible metal(1a), and the central capillary was also filled with fusible metal(1a). The tube was then ground down on a glass surface with graded emery and turpentine until the end was satisfactorily smooth and plane. (The process is considerably assisted by the addition of a little camphor to the turpentine.) It is on occasion found that the fusible metal is strongly adsorbed at the surface of the capillary and an application of hot acid is necessary to clean the latter. The joint shown at *J* in Fig. 1 considerably facilitates the cleaning of the apparatus; it need hardly be said that this joint must be air-tight, and in our own apparatus the fit was so good that the apparatus could be left for half an hour under a pressure of 5 cm. of aniline without showing any appreciable signs of leakage.

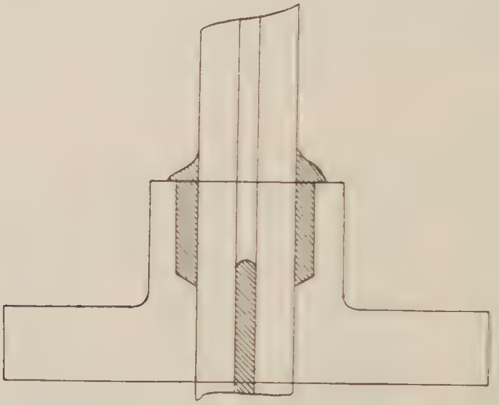


Fig. 2.

The formula for computation is

$$\rho h = \rho_1 (h_1 - r/3) + 2\gamma/gr.$$

It therefore follows that a plot of ρh as y against $(h_1 - r/3)$ as x gives a straight line. The slope of this line at once gives ρ_1, and the intercept gives $2\gamma/gr$ from which the surface tension γ may be deduced.

§ 3. THEORETICAL

The problem of the determination of the shape of the capillary surface inside a cylindrical tube of small radius has attracted considerable attention. Laplace(2), Poisson(3), Mathieu(4) and the late Lord Rayleigh(5) are among those who have developed formulae appropriate to this case. At the outset it is necessary to give a clear definition of the term "small," inasmuch as a considerable amount of confusion exists concerning the limits of applicability of such formulae. Thus Richards and Coombs(6) have made careful measurements of the surface tension of benzene and other liquids by the capillary rise method and, disturbed by the fact that certain formulae of approximation give impossible results when used outside the limits for which the approximation is valid, have, after indulging in "some mild reflections on the inadequacy of the help afforded by mathematics(5)" fallen back on an empirical correction to the simple formula.

If we introduce the convenient notation $a^2 \equiv \gamma/g\rho$, so that a is a quantity having the dimensions of a length, the simple formula

$$\gamma = \tfrac{1}{2}g\rho rh$$

becomes

$$rh = 2a^2.$$

The criterion of smallness of the radius of the tube is the value of the ratio r/h or of r^2/a^2, and the experimental conditions are so chosen that the formulae employed may be developed in ascending powers of r/h. Paying due regard, then, to the accuracy with which the experimental quantities may be determined, the lowest power of r/h which may be neglected in comparison with unity is readily observed.

In Fig. 3 below, taking an origin as shown, we have at the point P, with the notation as in the figure,

$$1/R_1 + 1/R_2 = (y + h)/a^2 \qquad \text{......(1).}$$

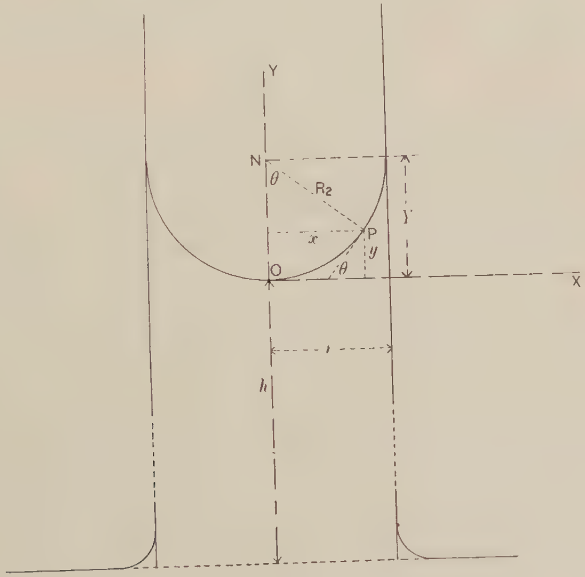


Fig. 3.

Now, R_1 is the radius of curvature of the meridional curve OP and is equal to $ds/d\theta$. R_2 is the second principal radius of curvature and is equal to $x/\sin\theta$. Substituting and reducing, we obtain

$$d\,(x \sin\theta)/dx = x\,(y + h)/a^2 \qquad \text{......(2)}$$

as the differential equation to the curve. In what follows we shall consider that the contact angle of the liquid with glass is zero.

If we assume that y/h is always negligible in comparison with unity, two integrations of (2) show that the equation to the meridional curve is a circle. If we now assume that the meridional curve deviates only slightly from the circular outline so that we may write

$$y = c - \sqrt{c^2 - x^2} - \psi,$$

where ψ is always small and is a function of x, Minchin(7) shows quite simply, by a modification of Laplace's original method, that

$$y = c - \sqrt{c^2 - x^2} + (c^3/3a^2) \log_e \{(c + \sqrt{c^2 - x^2})/2c\} \qquad \text{......(3)}.$$

For a liquid of zero contact angle it is obvious that c must be identified with r, the radius of the tube, and (3) becomes

$$y = r - \sqrt{r^2 - x^2} + (r^3/3a^2) \log_e \{(r + \sqrt{r^2 - x^2})/2r\} \qquad \text{......(4)}.$$

If we put $y = 0$ in (1), R_1 and R_2 become equal and the height h to which the liquid ascends in a tube of radius r is accurately given by

$$2/R = h/a^2 \qquad \text{......(5)},$$

where R is the radius of curvature of the meridional curve at its vertex. R is consequently given by

$$(d^2y/dx^2)^{-1}_{x=0},$$

which value, worked out from (4) and substituted in (5), gives

$$rh = 2a^2 (1 - r^2/6a^2) \qquad \text{......(6)},$$

the corresponding value of R being given by

$$R = r (1 + r^2/6a^2) \qquad \text{......(7)}.$$

If we desire a still closer approximation, it is most readily obtained by equating the weight of liquid raised to $2\pi r\gamma$. This gives

$$2\pi r\gamma = \pi r^2 h\rho g + V\rho g \qquad \text{......(8)},$$

where V is the volume of liquid in the meniscus. But if Y, Fig. 3, is the ordinate corresponding to $x = r$,

$$\begin{aligned} V &= \pi r^2 Y - \int_0^Y \pi x^2 \, dy \\ &= \pi r^2 Y - \int_0^r \pi x^2 (dy/dx) \, dx \qquad \text{......(9)}. \end{aligned}$$

Substituting the value of dy/dx obtained from (4) and remembering that when $x = r$, equation (4) gives

$$Y = r - (r^3/3a^2) \log_e 2 \qquad \text{......(10)},$$

we find that

$$V = \tfrac{1}{3}\pi r^3 - (\pi r^5/6a^2)(2 \log_e 2 - 1) \qquad \text{......(11)}.$$

Substituting in (8) we find that

$$2a^2 = rh + r^2/3 - (r^4/6a^2)(2 \log_e 2 - 1),$$

or

$$rh = 2a^2 [1 - r^2/6a^2 + (r^4/12a^4)(2 \log_e 2 - 1)] \qquad \text{......(12)}.$$

Written in ascending powers of r/h the equations for a^2, arranged in an ascending order of closeness of approximation, thus become

$$2a^2 = rh \qquad \text{......(13)},$$

$$2a^2 = rh\,(1 + \tfrac{1}{3}\,r/h) \qquad \text{......(14)},$$

$$\begin{aligned} 2a^2 &= rh\,[1 + \tfrac{1}{3}\,r/h - (r^2/3h^2)\,(2\log_e 2 - 1)] \\ &= rh\,[1 + \tfrac{1}{3}\,r/h - 0{\cdot}1288\,r^2/h^2] \end{aligned} \qquad \text{......(15)}.$$

This last equation agrees exactly with that arrived at by a considerably longer analysis by Poisson. Rayleigh's result, which is carried far enough to include a term r^3/h^3, also agrees with equation (15).

To obtain the corresponding approximations for the radius of curvature at the vertex, we note that, *exactly*,

$$2a^2 = Rh.$$

Hence from (12)

$$r = R\,[1 - r^2/6a^2 + (r^4/12a^4)\,(2\log_e 2 - 1)]$$

and the successive approximations for R become

$$R = r \qquad \text{......(16)},$$

$$R = r\,(1 + r^2/6a^2) \qquad \text{......(17)},$$

$$R = r\,[1 + r^2/6a^2 - (r^4/12a^4)\,(2\log_e 2 - \tfrac{4}{3})]. \qquad \text{......(18)}.$$

Turning to Fig. 2, we see that if R be the radius of curvature of the vertex of the meniscus, which is forced down to the lower end of the capillary immersed to a depth h_1 in the liquid of density ρ_1,

$$2\gamma/R = g\,(\rho h - \rho_1 h_1) \qquad \text{......(19)}.$$

With the tubes employed it is sufficient for our purpose to assume that R is given by equation (17). We obtain

$$2\gamma = gr\,(\rho h - \rho_1 h_1) + g\rho_1 r^2/3 \qquad \text{......(20)},$$

or putting b for $2\gamma/gr$, we have

$$\rho h = \rho_1\,(h_1 - r/3) + b \qquad \text{......(21)},$$

and a plot of ρh as y against $(h_1 - \tfrac{1}{3}r)$ as x gives the value of ρ_1 and of γ for the liquid under test.

§ 4. EXPERIMENTAL RESULTS

Experiments have been carried out on benzene, toluene, acetone, carbon tetrachloride and water. The substances were of first grade research quality and were free from the common impurities. The work was carried out at room temperature, which remained sensibly constant during the half-hour required to take any one set of observations. Tables 1 and 2 below give full details of two typical sets of readings. Three tubes were used during the whole series of experiments having radii of 0·0488 cm., 0·0354 cm. and 0·0237 cm. respectively. From numbers such as those shown in Tables 1 and 2, the graphs of Figs. 4 and 5 were obtained.

Fig. 4 shows, on a large scale, graphs obtained for acetone and for toluene, and Fig. 5 shows the graphs obtained for benzene and for carbon tetrachloride with each of the three tubes. The group of lines for each substance should, of course, be parallel as the slope is a measure of the density of the liquid concerned. Table 3 gives a conspectus of the results. It must be remembered that the production of authoritative figures is not our primary object, and that the substances used would require purification by redistillation or recrystallisation before any quantitative comparisons of a high degree of accuracy could be drawn.

Table 1. Experimental results for benzene

Temperature, 9·95° C. Density of manometer liquid, 1·030 gm./c.c.
Radius of tube, 0·0354 cm.

Readings for h_1			Readings for h			$h_1 - r/3$	ρh
Needle point	End of tube	h_1	Open end	Closed end	h		
9·104	8·696	0·408	6·159	4·240	1·919	0·396	1·976
9·328	8·696	0·632	6·245	4·145	2·100	0·620	2·163
9·585	8·696	0·889	6·345	4·016	2·329	0·877	2·399
10·022	8·696	1·326	6·527	3·848	2·679	1·314	2·759
10·212	8·696	1·516	6·640	3·770	2·870	1·504	2·956
10·428	8·696	1·732	6·717	3·674	3·043	1·720	3·134
10·726	8·696	2·030	6·844	3·526	3·318	2·018	3·417
10·895	8·696	2·199	6·902	3·479	3·423	2·187	3·526

Table 2. Experimental results for carbon tetrachloride

Temperature, 11·8° C. Density of manometer liquid, 1·029 gm./c.c.
Radius of tube, 0·0488 cm.

Readings for h_1			Readings for h			$h_1 - r/3$	ρh
Needle point	End of tube	h_1	Open end	Closed end	h		
5·811	5·552	0·259	5·911	4·410	1·501	0·243	1·545
6·104	5·552	0·552	6·140	4·180	1·960	0·536	2·017
6·274	5·552	0·722	6·274	4·048	2·226	0·706	2·291
6·453	5·552	0·901	6·422	3·898	2·524	0·885	2·597
6·654	5·552	1·102	6·577	3·742	2·835	1·086	2·917
6·815	5·552	1·263	6·708	3·612	3·096	1·247	3·186
7·140	5·552	1·588	6·957	3·361	3·596	1·572	3·700
7·328	5·552	1·776	7·106	3·216	3·890	1·760	4·002

§ 5. CONCLUSION

To sum up: the method, as the graphs of Figs. 4 and 5 show, is very self-consistent. It is reasonably rapid—about a half-hour suffices to take a set of readings—and while, in common with all capillary rise methods, it takes no account of the possible existence of a contact angle, it overcomes a number of the practical difficulties which are inherent in the ordinary practice of that method.

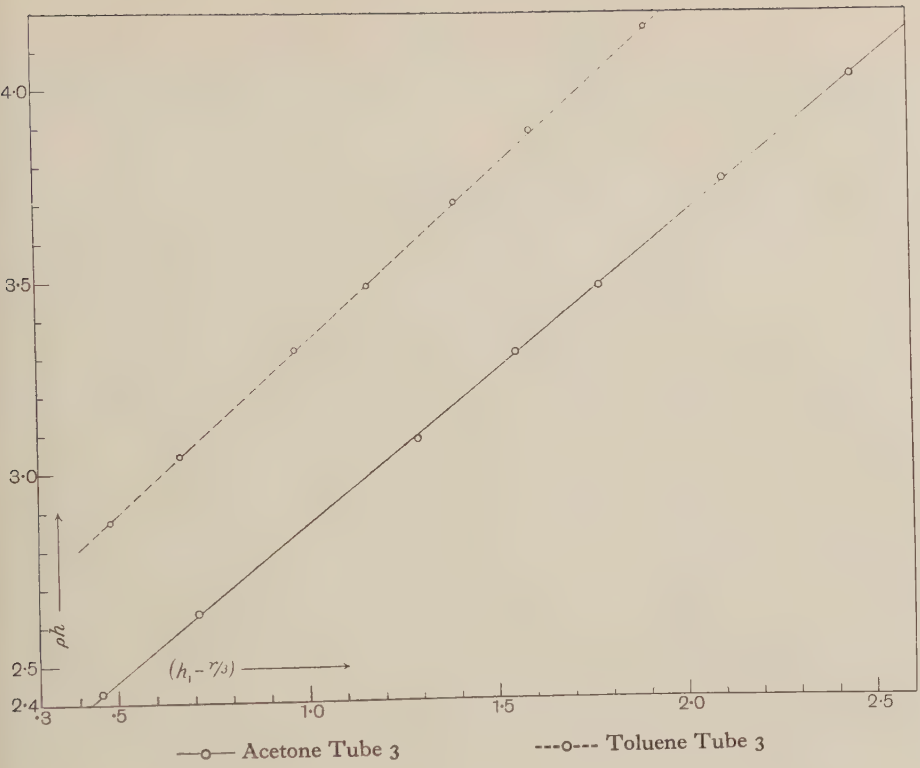

4·0
3·5
3·0
2·5
2·4
ρh
(h₁ - r/3)
·3
·5
1·0
1·5
2·0
2·5
—o— Acetone Tube 3
---o--- Toluene Tube 3

Fig. 4.

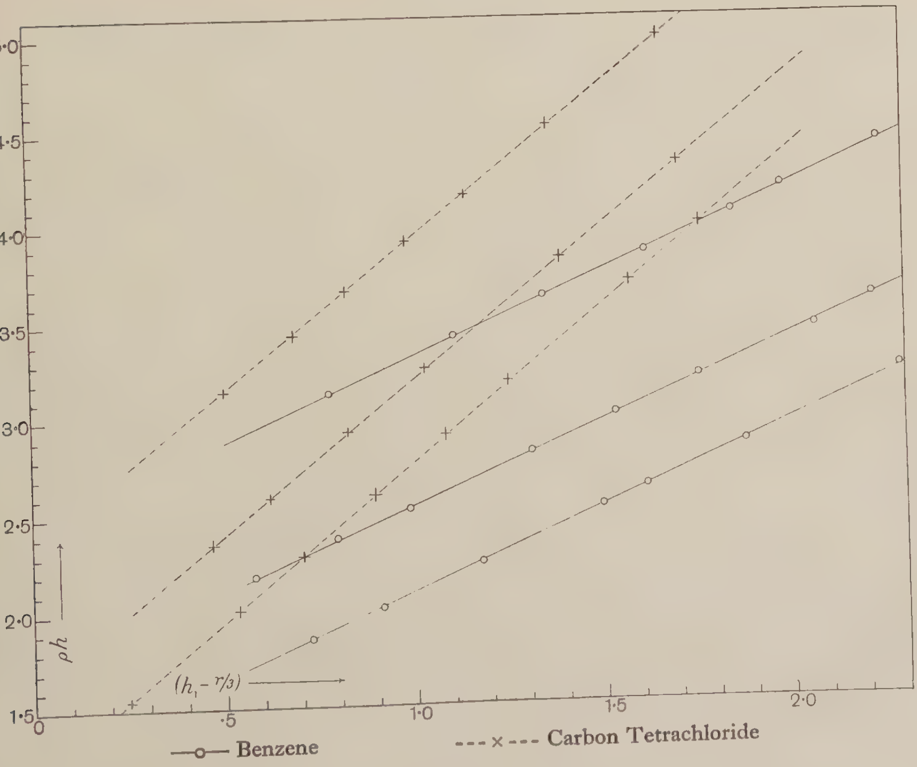

5·0
4·5
4·0
3·5
3·0
2·5
2·0
1·5
ρh
(h₁ - r/3)
0
·5
1·0
1·5
2·0
—o— Benzene
---×--- Carbon Tetrachloride

Fig. 5.

With a change of sign of the $r/3$ term, the method can be applied to the determination of the surface tension of a very small quantity of liquid⁽⁸⁾.

Table 3. Conspectus of results

Substance	Radius of tube	θ (° C.)	γ_θ	γ_{15}	ρ_1 from graph	ρ_1 S.G. bottle
Benzene	0·0488	16·5	28·94	29·19	0·884	0·8814
	0·0354	16·0	28·97	29·12	0·887	0·8818
	0·0237	16·0	28·47	28·62	0·879	0·8818
Toluene	0·0488	12·1	28·61	28·17	0·870	0·8728
	0·0354	12·0	28·91	28·47	0·867	0·8729
	0·0237	10·3	28·61	28·17	0·866	0·8744
Acetone	0·0488	10·1	24·03	23·43	0·809	0·8034
	0·0354	10·3	24·52	23·92	0·791	0·8032
	0·0237	11·0	23·81	23·33	0·796	0·8026
Carbon tetrachloride	0·0488	11·8	27·36	26·98	1·640	1·603
	0·0354	11·6	27·90	27·45	1·600	1·608
	0·0237	12·8	27·26	27·00	1·600	1·606
Water	0·0488	12	73·98	73·54	1·000	—
	0·0354	19	72·64	73·23	1·006	—
	0·0237	17·7	71·14	71·54	1·006	—

It is our pleasant duty to thank Professor C. H. Lees for the facilities which he has placed at our disposal.

REFERENCES

(1) Ferguson and Dawson. *Manchester Memoirs*, **65**, no. 5 (1921).
(1 *a*) Harkins and Brown. *Journ. Am. Chem. Soc.* **40**, 499 (1919).
(2) *Mécanique Céleste*. Supp. au Xᵉ Livre (1805).
(3) *Nouvelle Théorie de L'Action Capillaire*, chap. 4 (1831).
(4) Mathieu. *Théorie de la Capillarité*, chap. 2 (1883).
(5) Rayleigh. *Proc. Roy. Soc.* (A), **92**, 184 (1915).
(6) Richards and Coombs. *Journ. Am. Chem. Soc.* **37**, 1656 (1915).
(7) Minchin. *Hydrostatics*, p. 360 (1892).
(8) Ferguson. *Proc. Phys. Soc.* **36**, 37 (1923).

DISCUSSION

Prof. C. H. Lees: We have learned to look to Dr Ferguson for guidance in questions relating to surface tension, and I should like to ask him whether the results for water, which show a decrease of the surface tension as the size of the tube decreases, are sufficiently accurate to be taken as indicating some influence of the walls of the tube on the properties of the surface film.

Mr A. G. Tarrant: I should be glad if Dr Ferguson would tell us whether, in the method under discussion, the position of the meniscus at the lower end of the tube can be located with an accuracy comparable with that obtained in the method, described by him some years ago, in which a small drop of liquid is pressed down in a capillary tube till its lower surface is plane. As I have used this latter method with excellent results, I should be glad to know whether the present method is capable of equal precision.

Dr D. Owen pointed out that the title of the paper referred to the determination of density as well as surface tension. Could the method be regarded, however, as giving a measure of density sufficiently accurate for practical purposes?

Author's reply: I should not like to assume without more extended evidence that the variation mentioned by Prof. Lees was due to adsorption. The question raises an interesting point—that of the determination of the amount of adsorption at a liquid-glass surface by working with a narrow capillary tube in the form of a vertical grid, so that a relatively large surface may be exposed to adsorbent action before the capillary height is finally measured.

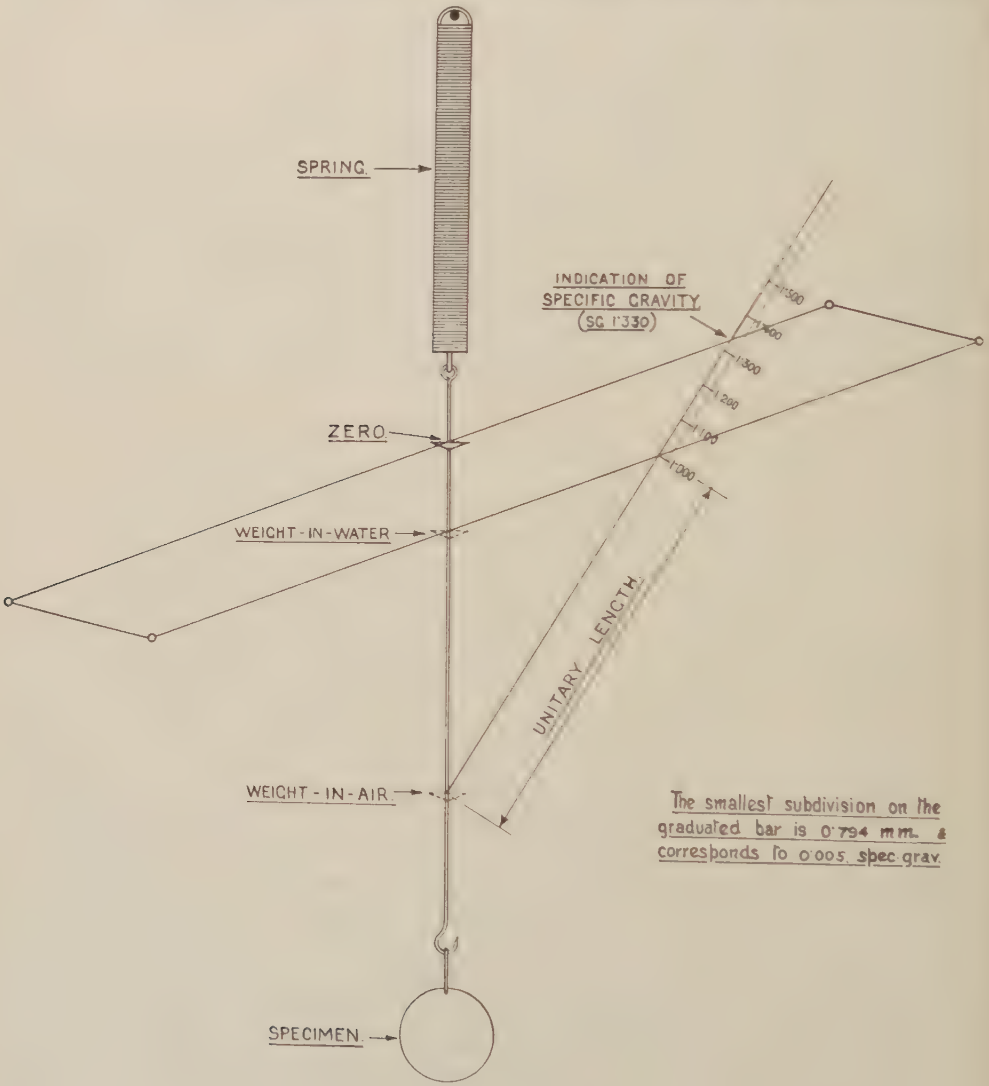
The two settings mentioned by Mr Tarrant may be made with about the same order of exactness—both are quite sensitive and satisfactory.

Like the titles of some works of higher art, the titles of scientific papers need not always be taken *au pied de la lettre*. The paper shows, I think, sufficiently well that the surface tension is the important factor, the density determination being of secondary importance—indeed the method may be considered as one which obviates the necessity for a density determination of the liquid under test; this consideration applies with special force to the experiments mentioned by Mr Tarrant, where the direct determination of the density of a cubic millimetre or thereabouts of liquid would not be an easy matter.

DEMONSTRATIONS

"An Instrument for the Rapid and Accurate Determination of the Specific Gravity of Solid Bodies." Demonstration given by W. A. BENTON, Head of Research Department, W. and T. Avery, Ltd., on February 8, 1929.

This instrument has been designed to enable the relative density of small samples of solid substances to be determined with extreme rapidity and to a high degree of accuracy. The model exhibited to the Society was fitted with a graduated



The smallest subdivision on the graduated bar is 0·794 mm. & corresponds to 0·005 spec. grav.

Fig. 1. Theoretical diagram.

scale specially adapted to indicate the specific gravity of light substances such as samples of rubber not exceeding a density of 2.

In order to obtain the required rapidity of operation it appeared necessary firstly to make the weighing in air and water automatic by means of a spring or pendulum resistant, so as to avoid the use of weights, and secondly to dispense with all recording of weights and arithmetical operations, as these greatly increase the risk of error and the expenditure of time required for a determination. A spiral spring resistant has been chosen as being intrinsically much more sensitive than any form of pendulum balance. Owing to the rapidity of the observations, errors due to temperature changes or spring hysteresis do not arise.

The spiral spring used in the instrument has suspended from it a light vertical wire to which is attached a thin circular disc, the sharp edge of which serves as an indicator. The wire terminates in a hook carrying the specimen. The extension of the spring from the zero position of the indicator gives the weight in air, the weight in water, and the difference, namely, the weight of the water displaced. No graduated scale is used in this portion of the instrument.

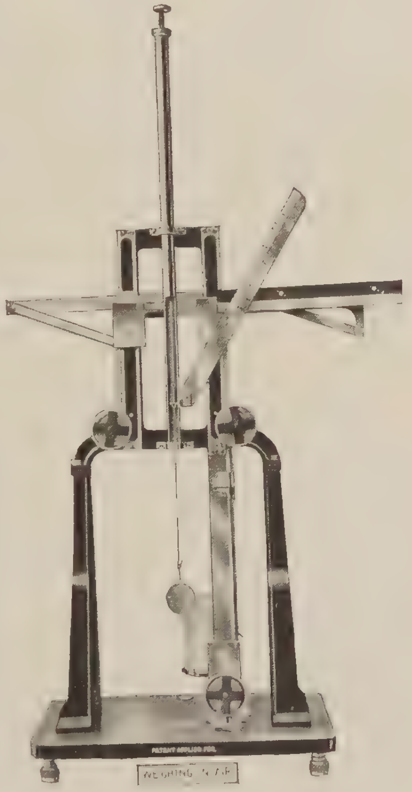


Fig. 2. Instrument for determining the specific gravity of solid bodies.

To perform the operation of dividing the weight in air by the weight of displaced water a special device has been adopted. An inclined bar suitably graduated can be moved vertically so that its zero point can be brought to coincide with the weight-in-air position of the resistant pointer. The fixed unitary length marked off on this inclined bar is always equated to the weight of water displaced by causing the lower member of a parallel rule to pass through the unitary point and through the weight-in-water indication. The upper member of this parallel rule is always slidably located on a knife-edge corresponding in position with the zero of the resistant indicator. This upper member will, therefore, by the principle of similar triangles, cut off from the inclined graduated bar a length proportional to the weight in air, and the number engraved on the graduated bar at the point where the upper member of the parallel rule cuts it will express the relative density of the body under examination. Fig. 1 will make the action of the instrument clear.

To make a determination the zero reading of the instrument must be adjusted by means of the screw at the top of the vertical tube containing the spring resistant. The body to be examined is then hung on the hook attached to the spring. By the turning of the milled knob on the right the pointer attached to the inclined graduated bar is brought into coincidence with the pointer of the spring resistant—now indicating the weight of the body in air. A beaker containing water is raised into position by the turning of another knurled knob at the base of the instrument, thus giving the weight in water. By means of a third knurled knob on the left of the instrument a knife-edge, on which the bottom member of the parallel rule is adapted to slide, is moved to coincide with the weight-in-water indication of the spring resistant. This lower member is pivoted to the inclined graduated bar so that it always passes through the unitary point. The specific gravity can then be read directly on the graduated bar at the point of intersection of the same with the upper member of the parallel rule.

To obtain optimum conditions the graduated scale in the model demonstrated to the Society has a long unitary length, but a scale can readily be fitted to deal with minerals, ores, alloys and other bodies of high specific gravity. Additional springs can be used in dealing with heavy samples. It is easy to obtain determinations accurate to about 0·002, the smallest sub-division being 0·005. A skilled operator can obtain a determination correct to approximately 0·005 in about 30 seconds. In fact, accurate weighing with a first-class balance is necessary to discover any error in the readings of the instrument.

"A Standard Electrostatic Voltmeter and Wattmeter used for Measurements of Alternating Currents at Power Frequencies at the National Physical Laboratory." Demonstration given by Dr E. H. RAYNER, on February 22, 1929.

The construction of some new apparatus for extending our equipment for alternating current measurements at power frequency provides an opportunity of showing the apparatus before it is installed. The principal instruments are an electrostatic voltmeter indicating up to about 120 volts on a scale about 18 ft. long, and a quadrant electrometer designed for use as a wattmeter and having a similar scale. They are of the type used as the national standards for such work, in which accuracy is of primary importance. As regards sensitivity they must be considerably superior to the commercial apparatus the errors of which it is their purpose to determine. The voltmeter is used commonly at 100 or 110 volts, higher voltages being measured on accurate potential dividing resistances. At 100 volts the scale divisions are about 80 mm. per volt, enabling values to be measured to 0·01 volt over a large part of the range of the instrument. The latter is of the multicellular type, with "needles" specially shaped to open up the bottom and top parts of the scale, which are normally much more contracted than the middle part. The suspension is a bifilar one, fine tungsten wire being used in it. A horizontal aluminium disc in oil provides the damping.

The wattmeter is a more delicate instrument, the torque available being much less than in the case of the voltmeter. Its nominal range is 100 or 110 volts on the "needle" and 2 volts on the quadrants. The needle is of thin aluminium alloy with stiffening ribs which have been pressed up in it by means of a grooved metal die. Blotting paper is used to press the metal foil into the die under pressures up to 10 tons. No oil damping is permissible. The separation of the quadrants is about 2 mm., and this is sufficiently small to provide, with the grooving of the needle, the necessary amount of air damping. The separation naturally affects the sensitivity, so that the sensitivity, damping and grooving are interdependent. The scale deflection with 100 volts on the needle and 2 volts on the quadrants is about 12 ft. Mechanical adjustments are provided for levelling the quadrants and varying their separation, and for moving them round inside the casing so that they can be oriented in any desired direction as regards the position of the needle. The insulation is made of "amberite." Special calibrating resistance boxes are made for the voltmeter and wattmeter, and selector switches are also required, the one for the wattmeter being of some elaboration, since the needle and quadrants must never be open circuited in passing from one method of connection to another or from one circuit to another.

REVIEWS

Physics in Industry. (1) No. 12, *The Physicist in the Glass Industry*, by Prof. W. E. S. Turner, O.B.E., D.Sc., F.Inst.P.; (2) No. 13, *Physics in the Food Industry*, by Sir William Hardy, M.A., F.R.S.; (3) No. 14, *The Physics of Photography*, by C. E. Kenneth Mees, D.Sc. (Institute of Physics, 1 Lowther Gardens, Exhibition Road, London, S.W. 7.) Paper covers, 1*s*. net each.

(1) This lecture commences with an historical introduction containing a timely reminder to professional physicists that much valuable work in the glass industry has been done by practical but untrained men. In fact, there was no academic institution for the scientific investigation of glass prior to 1915; since which date, however, much progress has been made in industrial laboratories.

Prof. Turner gives a very informative survey of the physical methods involved, and a few of the topics discussed may be briefly mentioned: (*a*) viscosity determinations by S. English, of whose apparatus a diagram is given without explanation, although the results are summarized; (*b*) relation between mobility and temperature, and the importance of annealing processes; (*c*) optical examination of specimens in polarized light; (*d*) variation of thermal expansion and electrical conductivity with amount of soda and potash present; and (*e*) connection between optical properties and composition. Finally an interesting comparison is made of the limits of transmission of vita-glass and other glasses. Convex glass is said to have a transmission in the ultra-violet as high as that of fused quartz.

(2) The problems of the food industry in which physicists have had some share appear to be those of the control of temperature, humidity and the composition of the air in an attempt to keep the food organisms alive. Uniformity of temperature throughout a space does not seem yet to be attainable.

There is not at present a science of smell, so that a smell cannot be expressed as a number, but Sir William Hardy puts in a strong plea for a method of measuring the concentration of odours. No exact work has been done on the absorption of odours because of the difficulty of measuring concentrations. This subject is of importance in the storage of eggs for example. According to the author much work also remains for the physicist in the problems of conduction in the pipes of cold-storage systems. The remainder of the paper is of a more biological nature, describing the effects of freezing and de-hydration on animal and vegetable tissues.

At the conclusion of a very readable survey reference is made to experiments on cohesive attraction, but the evidently simple diagram mentioned on p. 20 is missing.

(3) This is an important and well-illustrated paper read by the Director of the Kodak Research Laboratory before the Institute of Physics and the International Congress of Photography in July 1928. Some account is given of the progress which has been made in recent years in extending the spectral sensitivity of photographic materials. The methods of studying the relationship between density and exposure both for photographic plates and for printing papers are explained as a preface to a description of the graphic solution of "tone reproduction." There is then a discussion of the "sharpness" of the image, and the common impression that a small grain-size necessarily gives sharpness is corrected.

Other information of great importance to the physicist is contained in an account of the distortion of images of small size. Thus, two neighbouring images become oval in form and appear to attract one another, owing to the spreading of the light in the film. Displacement may also be produced by contraction of the gelatine, and an apparent repulsion between two images appears to be due to local exhaustion of the developer.

It was known, for example, that a weak component between two strong components of a spectral line would not be recorded on a photographic plate, and obviously the similar facts enumerated above are of primary importance to all those who rely on photographic plates for accurate measurements.

These publications may be very strongly recommended to the notice of all scientific workers who desire to know of the methods employed in the varied fields of industrial research and to envisage the problems which still demand investigation with all the help that physical knowledge can give.

J. E. C.

Physics in Astronomy, by Sir FRANK DYSON, K.B.E., F.R.S. (Presidential Address to the Institute of Physics, 1 Lowther Gardens, Exhibition Road, London, S.W. 7.) Paper covers, 1*s*. net.

In this pamphlet, which is largely historical, there is an account of the development of time measurement, with an interesting description of the wireless broadcasting of time signals.

Reference is made to the Shortt clock, which is almost a perfect time keeper except that there is a slight increase in its losing rate. Some new material for the pendulum rod is called for.

Questions perhaps of more interest to the physicist are the development of astrophysics, the Zeeman effect in sun spots, the use of the interferometer for the measurement of giant stars, and the determination of the solar constant. It is very kind of the Astronomer Royal to say that in spectroscopy "an astronomer must be to some extent a physicist if he is to get results of the necessary accuracy."

The whole paper makes delightful reading.

J. E. C.

Matter, Electricity, Energy (*The Principles of Modern Atomistics and Experimental Results of Atomic Investigation*) by WALTER GERLACH. Translated from 2nd German edition by F. J. FUCHS. Pp. xii + 428. (London: Chapman and Hall, Ltd.) 30*s*. net.

Despite the tragic fate that must inevitably overtake a book on modern physics—for the kaleidoscopic rapidity with which our outlook is changing puts such a work out of date by the time it has appeared on the market—there is no lack of writers who seek to make as plain as may be this fascinating but breathless tale.

Prof. Gerlach's book covers a wide field and is written to make a special appeal, not necessarily to the trained physicist, but to the engineer, the chemist, the naturalist, and to those students of science whose work lies outside the realm of pure physics, and who feel keenly that the changing outlook of the workers in physical science may have important reactions on their own work.

This review would become a catalogue if one were to quote fully the headlines of the thirty more or less independent lectures which make up the book. There is, as one would expect, much stress laid on the experimental side of "atomistics"; and isotopy, atomic rays, disintegration, the electronic charge, the magneton, super-conductivity, various and varied spectrum studies, the photo-electric effect, radiation measurements and, finally, atomism and macrocosm form but a section of the topics treated.

Does the book fulfil its purpose? With a certain amount of qualification, we may say that it does. The experimental side, as one would expect, is well and fully treated, and there is, of set purpose, an almost complete absence of mathematical proofs in the book. This is, we feel, an error of policy, for a simple mathematical exposition saves an immense mass of verbiage, and nowadays mathematical knowledge forms an essential part of the equipments of the chemist, the engineer and even of the naturalist.

The author has sought a certain measure of stability for his work by concentrating on fundamentals, but changes will happen for all that, and even in the matter of fundamentals there has been a great alteration in outlook since 1926; but, making due allowance for this and for the prolixity involved in the non-mathematical treatment of the topics, we feel justified in saying that each of the lectures forms a very convenient centre from which to proceed to wider discussion and reading.

The translation reads a trifle heavily. Archaic words such as "impartation" (p. 185) give an almost theological flavour to certain parts of the exposition, and (p. 164) "Boltzmann's equation P prop. $e^{-E/KT}$ enables us to state..." is jargon.

A. F.

The Origins and the Growth of Chemical Science by J. E. MARSH. Pp. x + 162. (London: John Murray.) 5*s*. net.

Mr Marsh is not in the position of the Needy Knife-Grinder—"Story, God bless you, I have none to tell, Sir"—he has an interesting tale to tell, and he tells it in an interesting manner. He does not, save in an incidental way, concern himself with origins, spending much more space on growth, sketching with clearness and philosophic breadth of view the development of chemical science from the far-off days of the four elements and the hypostatical principles, through the theories of phlogiston, salt-formation, radicals and types to these lively present times of co-valencies and contra-valencies, atomic numbers and isotopes.

The book is enlivened—though not overweighted—with touches of interesting biographical detail; and it is with more than academic interest that we look back to those robust days when Liebig, writing of Dumas' analysis of chloroform, could say "Wenn Herr Dumas erklären würde dass er ihn durch die Analyse und zwar mit Genauigkeit bestimmt habe, so halte ich das für Charlatanerie." Other times, other manners!

A. F.